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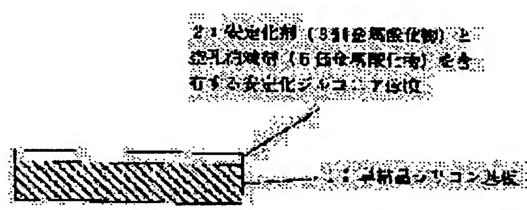
(71)Applicant : NISSAN MOTOR CO LTD
(72)Inventor : TANIMOTO SATOSHI

(54) THIN STABILIZED ZIRCONIA FILM/SINGLE-CRYSTALLINE SILICON SUBSTRATE LAMINATED STRUCTURE AND ITS PRODUCTION

(57)Abstract:
PROBLEM TO BE SOLVED: To produce a stabilized zirconia film/c-Si laminated structure free from ion drift.

SOLUTION: A thin stabilized zirconia (ZrO_2) film 2 is grown on a single- crystalline silicon semiconductor substrate 1 to obtain the objective laminated structure. The zirconia film 2 contains about equal amts. of a stabilizer made of oxide of a metal whose valence is lower than 4 as the valence of Zr and an oxygen ion hole vanishing agent made of oxide of a metal whose valence is higher than 4.



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(71)出願人　000003997
日産自動車株式会社
神奈川県横浜市神奈川区宝町2番地

(72)発明者　谷本　智
神奈川県横浜市神奈川区宝町2番地　日産自動車株式会社内

(74)代理人　弁理士　中村　純之助　（外1名）

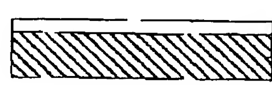
(54)【発明の名称】　安定化ジルコニア薄膜と単結晶シリコン基体との複合構造体およびその製造方法

(57)【要約】

【課題】イオンドリフトのない単結晶安定化ジルコニア膜／ｃ－Ｓｉ複合構造体およびその製造方法を提供する。

【解決手段】単結晶シリコン半導体基体１に安定化ジルコニア薄膜（ZrO_2）２を成長した複合構造体において、前記安定化ジルコニア薄膜がＺｒの原子価４価よりも低い原子価金属の酸化物からなる安定化剤と、前記Ｚｒの原子価４価よりも高い原子価金属の酸化物からなる酸素イオン空孔消滅剤とを概ね等量含有する、ことを特徴とする安定化ジルコニア薄膜と単結晶シリコン基体との複合構造体。

（図１）



【特許請求の範囲】
【請求項１】単結晶シリコン半導体基体に安定化ジルコニア薄膜（ZrO_2）を成長した複合構造体において、前記安定化ジルコニア薄膜がＺｒの原子価４価よりも低い原子価金属の酸化物からなる安定化剤と、前記Ｚｒの原子価４価よりも高い原子価金属の酸化物からなる酸素イオン空孔消滅剤とを概ね等量含有する、ことを特徴とする安定化ジルコニア薄膜と単結晶シリコン基体との複合構造体。
【請求項２】前記安定化剤の酸化物金属の価数が３価である場合、前記酸素イオン空孔消滅剤の酸化物金属の価数は５価である、ことを特徴とする請求項１に記載の安定化ジルコニア薄膜と単結晶シリコン基体との複合構造体。
【請求項３】前記の安定化剤がY_2O_3またはSm_2O_3であるか、あるいはY_2O_3とSm_2O_3の混合物であり、前記酸素イオン空孔消滅剤がTa_2O_5またはNb_2O_5またはV_2O_5であるか、あるいはTa_2O_5とNb_2O_5とV_2O_5のうちの２種以上を含む混合物である、ことを特徴とする請求項２に記載の安定化ジルコニア薄膜と単結晶シリコン基体との複合構造体。
【請求項４】前記安定化剤の酸化物金属の価数が２価である場合、前記酸素イオン空孔消滅剤の酸化物金属の価数は６価である、ことを特徴とする請求項１に記載の安定化ジルコニア薄膜と単結晶シリコン基体との複合構造体。
【請求項５】前記の安定化剤がCaO、前記酸素イオン空孔消滅剤がWO_3またはMoO_3で構成されることを特徴とする請求項４項に記載の安定化ジルコニア薄膜と単結晶シリコン基体との複合構造体。
【請求項６】前記安定化剤および酸素イオン消滅剤の濃度が５mol%～３０mol%の範囲の値である、ことを特徴とする請求項１乃至請求項５の何れかに記載の安定化ジルコニア薄膜と単結晶シリコン基体との複合構造体。
【請求項７】単結晶シリコン半導体基体に安定化ジルコニア薄膜を成長した複合構造体において、該安定化ジルコニア薄膜が該単結晶シリコン半導体基体にヘテロエピタキシャル成長している単結晶膜であることを特徴とする請求項１乃至請求項６の何れかに記載の安定化ジルコニア薄膜と単結晶シリコン基体との複合構造体。
【請求項８】前記請求項１乃至請求項７の何れかに記載の安定化ジルコニア薄膜と単結晶シリコン基体との複合構造体を製造する方法であって、
該単結晶シリコン半導体基体の表面の自然酸化膜を除去し、洗浄する工程と、
該洗浄後の基体を自然酸化膜を生成させることなく速やかに真空蒸着槽に装着し、10^{-8}Torr以下に排気する工程と、
該真空蒸着槽の中で電子ビーム蒸着法、イオンビームスパッタリング法、レーザアブレーション法の中から選ばれた一つの成膜方法で該単結晶シリコン基板上に安定化ジルコニア薄膜を形成する工程と、
を備えたことを特徴とする複合構造体の製造方法。
【請求項９】前記電子ビーム蒸着法、イオンビームスパッタリング法、レーザアブレーション法で使用される蒸着ターゲットが、前記安定化剤、酸素イオン空孔消滅剤、およびジルコニアの各粉末を所定に割合で混合したのち円盤状に加圧整形したものである、ことを特徴とする請求項８に記載の複合構造体の製造方法。
【請求項１０】前記各成膜方法による安定化ジルコニア薄膜の形成工程において、蒸着の初期は高真空中で成膜を行い、膜厚が概ね３ｎｍに達したところで、外部から蒸着槽に酸素、もしくはオゾンを含む酸素を導入し、引続き成膜を行うことを特徴とする請求項８または請求項９に記載の複合構造体の製造方法。
【請求項１１】前記請求項１乃至請求項７の何れかに記載の安定化ジルコニア薄膜と単結晶シリコン基体との複合構造体を製造する方法であって、
該単結晶シリコン半導体基体の表面の自然酸化膜を除去し、洗浄する工程と、
該洗浄後の基体を自然酸化膜を生成させることなく速やかに反応器に装着し、10^{-6}Torr以下に排気する工程と、
該反応器の中で化学気相成長法で該単結晶シリコン基板上に安定化ジルコニア薄膜を形成する工程と、
を備えたことを特徴とする複合構造体の製造方法。

【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明はイオンドリフトのない良好な安定化ジルコニア薄膜／単結晶シリコン複合構造体およびその製造方法に関するものである。
【０００２】
【従来の技術】ジルコニア：ZrO_2は融点が２７００℃と高く、機械的に強靭であるばかりでなく、化学薬品に対する強い耐腐食性を備え、優れた絶縁性と高い誘電率を有しているので、様々な産業分野で応用されている。純粋なジルコニアには３種類の多形、すなわち高温から立方晶、正方晶、単斜晶があることが知られているが、温度の低下によって対称性の低い晶系に相転位してしまうので、応用上有用な立方晶の単結晶は常温では得られない。しかし、これに２価や３価の金属酸化物を固溶させると、結晶が安定化され、高温相である立方晶域を室温付近まで下げることができる。以下このような立方晶系のジルコニアを「安定化ジルコニア」を総称することにする。
【０００３】安定化ジルコニアとして、イットリア：Y_2O_3で安定化させたイットリア安定化ジルコニア：ＹＳＺ（Yttria－Stabilized Zirconia）や、サマリア：Sm_2O_3で安定化させたサマリア安定化ジルコニア（ＳＳＺ）、あるいは、酸化カルシウムで安定化させたカルシ

ウム安定化ジルコニア（ＣＳＺ）などが報告されている。

【０００４】また、安定化ジルコニアの格子定数a_0＝０．５１～０．５２ｎｍは単結晶シリコン（立方晶）：ｃ－Ｓｉの格子定数a_0＝０．５４ｎｍに近いことから、近年、内外の研究者によってｃ－Ｓｉ基板上へエピタキシャル成長させることが研究され、すでに電子ビーム蒸着法、イオンビームスパッタリング法、レーザアブレーション法などの成膜手段で成功している。一例を挙げるならば、「Fukumoto等の“Japanese Journal of Applied Physics,” 27, 1988, L1404.」には電子ビーム蒸着法でＳｉ（１００）基板にｃ軸配向したＹＳＺエピタキシャル膜を生成することに成功した旨が報告されている。

【０００５】Ｓｉは一般的に他の材料と固相反応や相互拡散しやすく、また、酸化雰囲気では比較的容易に表面に無定形であるSiO_2を生成しやすいので、ヘテロエピタキシャル成長をさせることは容易ではない。したがって、Ｓｉ上に安定化ジルコニアがエピタキシャル成長できるという研究成果は新しいＳｉ半導体技術の開拓に極めて有益であった。

【０００６】また、安定化ジルコニアと他の或る一群の結晶との結晶学的関係において特筆するべきことは、安定化ジルコニアの<１１０>軸長の１／２の長さ（～０．３６ｎｍ）或いはａ軸長が、つぎのような立方晶あるいは正方晶結晶体のａ，ｂ軸長にほぼ等しい、という事実である。ここで一群の結晶体とは、①白金：Ｐｔ（a_0＝０．３９ｎｍ）やイリジウム：Ｉｒ（a_0＝０．３８ｎｍ）等の金属、②チタン酸鉛：$PbTiO_3$（a_0＝０．３９ｎｍ）やチタンジルコン酸鉛：$Pb(Zr_xTi_{1-x})O_3$（略称ＰＺＴ，a_0＝約０．３９ｎｍ）などの正方晶ペロブスカイト強誘電体、③酸化イットリウムバリウム銅：$YBa_3Cu_3O_{7-x}$（略称ＹＢＣＯ）などの正方晶高温超電導体、④$SrTiO_3$やBaF_2などの（常）誘電体、⑤ＳｉやＧｅなどの半導体、などである。

【０００７】上記の事実は安定化ジルコニア単結晶基板上にこれらの多様な材料をエピタキシャル成長できる可能性を示唆している。実際、単結晶（１００）ＹＳＺ基板上にはｃ軸配向の$YBa_3Cu_3O_{7-x}$（例えば G. A. Samara, Journal of AppliedPhysics, 68, 1990, 4214.）やＳｉ（例えばH. M. Masasevit et al., Journal of the Electrochemical Society, 130, 1983, 1752.）のエピタキシャル膜が得られている。また、本出願の発明者は最近実施した実験の中で、単結晶ＹＳＺ（１００）基板や単結晶ＳＳＺ（１００）基板上にエピタキシャル成長した$Pb(Zr_xTi_{1-x})O_3$膜とＰｔ膜（ともにｃ軸配向）を得ることに成功している。

【０００８】また、単結晶安定化ジルコニア基板に前記①～⑤のごとき様々な膜がエピタキシャル成長できるということは、単結晶安定化ジルコニア膜の上にも①～⑤の膜をエピタキシャル成長できることを意味する。こうして安定化ジルコニアという酸化物エピタキシャル膜を介して、単結晶Ｓｉ基板上に多種多様な単結晶薄膜材料をエピタキシャル形成することが可能になった。

【０００９】この新技術にいまもっとも注目しているのは以下に説明する機能性集積回路の分野である。近年、強誘電体薄膜、高温超電導体薄膜、半導体薄膜などの機能性材料を、Ｓｉ半導体集積回路基板に搭載しようとする意欲的な試みが活発に行なわれるようになってきた。これは、分極反転特性、焦電性、圧電性、超電導性、光・高温半導体特性といった、これまでの回路構成では達成できない特殊機能とＳｉ集積回路の高速演算処理を併せ持つ付加価値の高い機能性集積回路の実現を意図している。

【００１０】機能性薄膜は多くの場合、結晶体となった時、上述のような興味深い物性を示す。したがって、機能性集積回路において、その性能をもっとも効率よく、もっとも高感度に利用するためには、単結晶化させた膜を生成する技術が強く望まれている。また、強誘電体においては、その分極反転特性、焦電性、圧電性が強く結晶異方性を示すので、特性が現れる特定方向に配向させる工夫も必要である。一般的に言って、無定形基体や多結晶基体に単結晶膜を生成することは困難である。この問題を解決するために、成長しようとする単結晶膜の結晶構造（あるいは格子定数）と類似した結晶構造の基体を使用し、この上にヘテロエピタキシャル成長させる方法が知られている。機能性集積回路でこの方法を適用するには、唯一の単結晶体であるＳｉ基板を一部露出させ、ここを基体として、機能性デバイスを構築する。

【００１１】機能性デバイスの構造は様々であるが、応用例が多く実用上重要な構造は、絶縁膜（Ｉ）を形成したＳｉ基体（ＩＳ構造）に機能性薄膜やその他の膜を形成した構造のものである。たとえば、金属（Ｍ）－絶縁膜（Ｉ）－半導体（Ｓ）トランジスタの“Ｉ”部の上に少なくとも一層の強誘電体膜（Ｆ＝機能性薄膜）を含む積層薄膜体で置き換えたＭＦＩＳ型、あるいはＭＦＭＩＳ型の不揮発性メモリや焦電センサ、圧電センサなどはその好例である。また、低消費電力・高速演算を目指した高温超電導体（Ｆ）配線集積回路はもう一つの例である。ここで高温超電導体配線はコンタクト部を除いて絶縁体膜／Ｓｉ基板（ＩＳ構造）上に配設される。このほかに、単結晶Ｓｉ基板上に絶縁体膜を介して単結晶半導体膜（Ｆ＝Ｓ）形成したいわゆるＳＯＩ型ＭＯＳデバイスも一例に加えられよう。このデバイスは高速・高集積・高放射線耐性の集積回路を実現する上で極めて重要であり、その構造はＭＯＦ（＝Ｓ）ＩＳである。このようにＩＳ複合構造体は、Ｓｉ集積回路基板上に機能性薄膜や機能性デバイスを構築するための基本構造の一つである。

【００１２】このＩＳ構造基体に単結晶の機能性薄膜を

含む機能性デバイスを構築するためには、上部に形成する機能性薄膜まで、Ｓｉ基板の結晶性をヘテロエピタキシによって伝達する必要がある。このためには、少なくとも、Ｉ層はエピタキシャル成長させた絶縁膜である必要がある。前記の安定化ジルコニア膜（なかでも、ＹＳＺ膜）は、上記のような機能を満たすものであるため、注目を集めているのである。

【００１３】上記のように、安定化ジルコニア／ｃ－Ｓｉ複合構造体は機能性集積回路等を実現するための基体としての要件を備えているので極めて有用である。しかし、実際にこれを使用するためには、つぎに詳しく説明する「イオンドリフト」問題を解決しなければならない。

【００１４】図５は、Ａｌ電極膜／単結晶安定化ジルコニア膜／ｃ－ＳｉからなるＭＩＳ容量のＣ－Ｖ特性を様々な掃引速度ＳＲ（＝１～０．００１Ｖ／秒）に関して測定した結果を示す特性図である。図５の特性は、ゲートバイアス電圧の掃引は５Ｖに３０分間維持した後、０．１Ｖのステップで降圧方向に行い、－５Ｖに到達した時点で再び３０分間、電圧を維持し、その後、掃引方向を反転させ、５Ｖに向けて昇圧させた結果である。なお、測定周波数は１ＭＨｚの正弦波である。

【００１５】図５の結果において、降圧方向の特性と昇圧方向の特性とで、時計廻りのヒステリシスが生じているのが分かる。このヒステリシスは、単結晶安定化ジルコニア膜の中に電界によって移動可能なイオンが存在＊し、これがドリフトしていることを示すものである。なお、ＳＲ＞１Ｖ／秒のＣ－Ｖ特性（図示省略）はＳＲ＝１Ｖ／秒のそれと変わらない。また、ヒステリシスがＳＲ＝０．００５Ｖ／秒以下では消失していることから、可動イオンの応答は数秒～数１００秒の範囲に分布していることが理解される。以下、複合構造体のイオンドリフトの程度を測る目安として、イオンドリフト度：ΔＶ［Ｖ］なる量を定義する。ΔＶは、図５のような、ＳＲを変化させて得られたＣ－Ｖ特性の中で観察されたヒステリシスの最大幅である。

【００１６】最近のジルコニア研究によれば、このようなイオンドリフトは安定化剤の導入によってジルコニア結晶内に必然的に生じた酸素イオン空孔が、外部電界に誘引されて移動することによって起こることが知られている。これをもう少しくわしく説明すると、安定化ジルコニア：ＡＳＺ（Ａは安定化剤の金属元素）では、安定化剤の２価または３価の金属イオンA^{2+}、A^{3+}がZrO_2結晶の４価のZr^{4+}イオンと置換して陽イオン格子位置に入り、電気的中性を維持するために、添加量と置換したイオンの価数に応じて酸素イオン空孔：Ｖｏが形成される。このような格子欠陥の生成反応をＹＳＺおよびＣＳＺについて表すと、下記（化１）式に示すようになる。

【００１７】

【化１】

$$\mathrm{YSZ:}\quad Y_2O_3 \xrightarrow{ZrO_2} 2\,\overset{-}{Y}(Zr) + \overset{++}{V}o + 3\,Oo \qquad \cdots(化1)$$

$$\mathrm{CSZ:}\quad CaO \xrightarrow{ZrO_2} Ca\overset{--}{(Zr)} + \overset{++}{V}o + Oo \qquad \cdots(化2)$$

【００１８】ただし、Ｙ(Zr)：Ｚｒと置換したＹを表示

Ｃａ(Zr)：Ｚｒと置換したＣａを表示

「＋」：正の有効電荷数

「－」：負の有効電荷数

上記（化１）式から明かなとおり、Ｙのような３価の金属イオンが４価のＺｒイオンを２個置換すると１個の酸素イオン空孔が生成され、Ｃａのような２価の金属イオンがＺｒイオンを１個置換すると１個の酸素イオン空孔が生成される。この酸素イオン空孔は電界が印加されると、あたかも正の可動イオンのように振舞い、電界の方向に移動する。

【００１９】図６（ａ）～（ｃ）は、立方晶ＣＳＺ安定化ジルコニア単結晶を２次元模式図的に描いた図である。この中で“□”は酸素イオン空孔を表している。いま、紙面下から上に向かって正電界：Ｅが印加されると、酸素イオン空孔から見て電界下手の最近接酸素イオンが、空孔に向けて移動できるようになる。実際に移動すると、（ｂ）のように酸素イオン空孔は、元あった酸素イオンの位置に移動する。新しい位置に移った空孔に向かって、その下手にある最近接酸素イオンが（ｃ）のように再び移動する。このようにして酸素イオン空孔は電界の方向に移動するのである。電界があるとき、負電荷を帯びた酸素イオンが空孔を介して電界と逆方向に移動し、正電荷を帯びた空孔は相対的に電界の方向に向かって漂っていく。これがイオンドリフトである。

【００２０】

【発明が解決しようとする課題】このような安定化ジルコニア膜のイオンドリフト（存在と遅応答）は、下にあるＳｉ半導体基板の表面ポテンシャルや、上部に形成した機能性デバイスの特性を長時間（０．１秒～１０００秒）にわたって不安定にさせるので、極めて有害であり、単結晶安定化ジルコニア膜／ｃ－Ｓｉ複合構造体を基体にした機能性集積回路の実現の大きな妨げになっていた。

【００２１】本発明は、このような従来技術の問題点を解決するためになされたもので、イオンドリフトのない単結晶安定化ジルコニア膜／ｃ－Ｓｉ複合構造体および

その製造方法を提供することを目的としている。

【００２２】

【課題を解決するための手段】上記の目的を達成するため、本発明においては、特許請求の範囲に記載するように構成している。すなわち、請求項１に記載の発明においては、複合構造体の構造として、ｃ－Ｓｉ上にＺｒよりも高い原子価をもつ金属の酸化物（以下、空孔消滅剤と称する）を含有する新規な組成の単結晶安定化ジルコニアを配設する構成にしている。また、請求項２～請求項７に記載の発明は、請求項１の各構成要素の構成例を示すものである。

【００２３】また、請求項８～請求項１１は、上記複合構造体の製造方法の例であり、Ｓｉ半導体基体表面の自然酸化膜を除去した後、この上に電子ビーム蒸着法、あるいは、イオンビームスパッタリング、レーザアブレーション法、化学的気相成長法で安定化ジルコニア薄膜を形成する。

【００２４】本発明の安定化ジルコニア膜／ｃ－Ｓｉ複合構造体において、安定化ジルコニアに新規に添加する酸素イオン空孔消滅剤は、安定化ジルコニア膜の酸素イオン空孔を除去する作用をする。よって、ドリフトするべきイオン空孔が安定化ジルコニア結晶体の中からなくなるので、本発明は従来技術の問題点であったイオンドリフト問題を解決できる。さらに、安定化ジルコニア膜は空孔消滅剤を添加しても、依然、立方晶系の結晶構造ならびに品質を維持しているので、機能性材料を含む各種材料のエピタキシャル膜形成用基体としての機能は、なんら損なわれることはない。

【００２５】

【発明の効果】本発明によれば、単結晶シリコン半導体基体に立方晶安定化ジルコニア薄膜を成長した複合構造体において、安定化ジルコニア薄膜に、４価よりも低い原子価金属の酸化物からなる安定化剤と、４価よりも高い原子価金属の酸化物からなる酸素イオン空孔消滅剤と、を等量含有させる構成としたことにより、酸素イオン空孔が安定化ジルコニア薄膜から除去され、それによってイオンドリフト問題解決できる、という優れた効果が得られる。

【００２６】また、製造方法の第１の実施の形態（実施例３）に記載した電子ビーム蒸着装置を用いた方法においては、電子ビーム蒸着装置という安価な成膜手段によって安定化ジルコニアを形成しているので、他の成膜法に比べて、低価格で複合構造体を製造できるという利点がある。

【００２７】また、製造方法の第２の実施の形態（実施例４）に記載した方法は、他の実施例と比較して、４５０℃という低温で成膜できるので、成膜前に非耐熱性の材料や構造がＳｉ基体に形成されている場合には、極めて有効であるという特徴を有している。

【００２８】また、製造方法の第３の実施の形態（実施例５）に記載した方法は、安定化ジルコニア膜の金属元素の組成がターゲットの金属元素の組成に等しくなるという特質を備えているので、或るレーザアブレーション成膜装置で得た最適条件を他のレーザアブレーション成膜装置のものとして使用することが可能である。これは生産用の大規模成膜装置を立ち上げる際には、最適化に要する時間を省けるという有用性を発揮する。

【００２９】また、製造方法の第４の実施の形態（実施例６）は、微細な凹凸があるＳｉ単結晶基体でも被覆性の高い安定化ジルコニア膜を提供できるという優れた特徴がある。

【００３０】

【発明の実施の形態】以下、本発明にかかる安定化ジルコニア薄膜と基体との複合構造体の構成および該構成の製造方法の実施例を図を用いて詳細に説明する。なお、以下の図において同じ番号の対象物はすべて同じ物であって、一度詳細に説明した物は後の図においては簡単に説明するにとどめることにする。

【００３１】（１）複合構造体の第１の実施の形態　＜実施例１＞

図１は、本発明に係る複合構造体の第１の実施の形態を示す模式図的要部断面図である。図１において、１は単結晶Ｓｉ（１００）基板である。２は、立方晶エピタキシャル安定化ジルコニア薄膜であり、この中には３価の金属酸化物Y_2O_3またはSm_2O_3、あるいは、これら混合物からなる安定化剤と、５価の金属酸化物Ta_2O_5、Nb_2O_5、V_2O_5、あるいは、これら混合物からなる空孔消滅剤とが添加されている。安定化剤と空孔消滅剤の濃度は概ね等しく、５mol%～２５mol%の間である。安定化剤および空孔消滅剤はエピタキシャル成長時にその場で添加される。この立方晶エピタキシャル安定化ジルコニア薄膜２は電子ビーム蒸着法、イオンビームスパッタリング法、レーザアブレーション法、化学気相成長法の中から任意に選ばれた一つの方法でエピタキシャル成膜されるが、成膜法の詳細な説明は後述の製造方法の実施例の中で行う。

【００３２】（２）複合構造体の第２の実施の形態　＜実施例２＞

図２は、本発明に係る複合構造体の第２の実施の形態を示す模式図的要部断面図である。図２において、１は単結晶Ｓｉ（１００）基板である。２’は立方晶エピタキシャル安定化ジルコニア薄膜であり、この中には２価の金属酸化物ＣａＯからなる安定化剤と、６価の金属酸化物WO_3あるいはMoO_3からなる空孔消滅剤とが添加されている。安定化剤と空孔消滅剤の濃度は概ね等しく、８mol%～３０mol%の間である。安定化剤および空孔消滅剤はエピタキシャル成長時にその場で添加される。立方晶エピタキシャル安定化ジルコニア薄膜２’は電子ビーム蒸着法、イオンビームスパッタリング法、レーザアブレーション法、化学気相成長法の中から選ばれた一方

法でエピタキシャル成膜されるが、成膜法の詳細な説明は後述の製造方法の実施例の中で行う。

【００３３】（３）複合構造体の製造方法の第１の実施の形態　＜実施例３＞

ここでは図１に記載した複合体構造を電子ビーム蒸着法で実現する製造方法を説明する。まず、ＲＣＡ洗浄（アンモニア水と過酸化水素水の混合液による洗浄ＳＣ１と塩酸と過酸化水素水の混合液による洗浄ＳＣ２からなる伝統的なＳｉ基板洗浄法）と希フッ酸洗浄（５％濃度のＨＦ水溶液に数十秒浸漬した後、純水でリンスし乾燥する洗浄法）とでＳｉ基板１の表面の汚染物および自然酸化物を除去する。

【００３４】つづいてＳｉ基板１上に酸化イットリウムY_2O_3で安定化され、酸化タンタルTa_2O_5で空孔消滅された安定化ジルコニア膜２（以下ＹＳＺ：Ｔａのように略記する）を電子ビーム蒸着法にて形成する。蒸着のターゲットはY_2O_3粉末とZrO_2粉末とTa_2O_5粉末をモル比でｘ：（１－ｘ－ｙ）：ｙに混合し、ホットプレスで円盤状（直径１５mm、厚み７mm）に整形したタブレットである。ここでｘ＝約９％、ｙ＝約１５％である。タブレットのTa_2O_5のモル濃度がY_2O_3に比べて＊＊大きいのは、Ta_2O_5の蒸発がY_2O_3やZrO_2に比べて相対的に遅いという事情に基づいている。

【００３５】成膜の手順を説明すると、まず、ハース（＝タブレット充填場所）にタブレットを充填し、直ちに、上記洗浄したＳｉ基板１を蒸着槽中の基板ホルダに設置し、蒸着槽内を排気する。このホルダは基板を常温から１０００℃までの温度に加熱する能力を有しており、蒸着槽内のハースに収納された蒸着タブレットと十分な距離を置いて対抗している。蒸着装置の排気は強力であり、内部の圧力は10^{-9}Torr以下まで減圧することが可能である。蒸着槽の圧力が10^{-6}Torrに達したら基板温度を加熱して所定の成膜温度にする。温度が安定し、かつ、蒸着槽内の圧力が10^{-9}Torr以下に下がったところで蒸着電源の出力をオンして電子ビームをタブレットに射突させ蒸着を開始する。蒸着開始後、ＹＳＺの膜厚が概ね３ｎｍになったところで外部から高純度乾燥酸素を導入して圧力を2×10^{-6}Torrに調節すると共にフィラメント電流を増やして成膜を続ける。膜厚は成膜時間、成膜速度はフィラメント電流で決定する。

【００３６】典型的なエピタキシャルＹＳＺ：Ｔａの成膜条件はつぎのとおりである。

ＹＳＺ成膜条件

成膜圧力	1×10^{-8}Torr（膜厚３ｎｍまで）
	2×10^{-6}Torr（膜厚３ｎｍからO_2導入）
成膜温度	８００℃（基板温度）
ターゲット	Y_2O_3：ZrO_2：Ta_2O_5＝９：８１：８
投入電力	２００Ｗ
フィラメント電流	２０ｍＡ（初期）
	５０ｍＡ（膜厚３ｎｍから）
電子ビーム加速電圧	８ｋＶ

上記のようにして成膜し、膜厚が所望の値になったところで蒸着電源の出力を切って成膜を終える。この後、蒸着槽に基板置いたまま基板を徐冷し、基板温度が十分低くなってから基板を蒸着槽から取出す。

【００３７】このようにして堆積したＹＳＺ：Ｔａ膜の安定化剤と空孔消滅剤の濃度は、実験精度の範囲内で同濃度（＝１１％）であった。また、膜の結晶構造はホタル石構造（立方晶）を有する単結晶エピタキシャル膜であった（詳細は後述する効果の項で説明）。この製造方法は、電子ビーム蒸着装置という極めてありふれた安価な成膜手段によっているので、後述する他の成膜法に比べて、大面積のエピタキシャルＹＳＺ成膜が低価格でできる、という利点がある。また、上記の製造方法を用いて（ただし条件は若干異なる）、複合構造体の第２の実施の形態（実施例２）の構造も実現できる。

【００３８】（４）複合構造体の製造方法の第２の実施の形態　＜実施例４＞

ここでは図２に記載した複合構造をイオンビームスパッタリング法で実現する製造方法を説明する。まず、前記実施例３と同様にＲＣＡ洗浄と希フッ酸洗浄とでＳｉ基板１の表面の汚染物および自然酸化物を除去する。

【００３９】つづいてＳｉ基板１上に酸化カルシウムＣａＯで安定化され、酸化タグステンWO_3で酸素イオン空孔を消滅化させた安定化ジルコニア膜２’（以下ＣＳＺ：Ｗ）をイオンビームスパタリング法でＳｉ基板１に形成する。スパッタリングのターゲットはＣａＯ粉末とZrO_2粉末とWO_3粉末をモル比でｘ：（１－ｘ－ｙ）：ｙに混合し、ホットプレスで円盤状に整形したものである。ここでｘ＝約１１％、ｙ＝約１１％である。

【００４０】成膜の手順を説明すると、まず、ターゲットホルダにターゲットを設置し、前記洗浄直後のＳｉ基板１を蒸着槽中の基板ホルダに設置し、蒸着槽内を排気する。このホルダは基板を常温から６００℃までの温度に加熱する能力を有しており、ターゲットから約６０ｃｍの距離を挟んで対抗している。蒸着装置の排気は強力であり、内部の圧力は10^{-9}Torr以下まで減圧することが可能である。蒸着槽の圧力が10^{-6}Torrに達したら基板温度を加熱して所定の成膜温度にする。温度が安定し、かつ、蒸着槽内の圧力が10^{-9}Torr以下に下がったところでイオン源の電源の出力をオンにし、イオンビー

ムをタブレットに射突させ蒸着を開始する。蒸着開始後、ＣＳＺの膜厚が３ｎｍになるまでは少なくとも10^{-8}Torr台の高真空を保って成膜するが、３ｎｍを超えたところで外部から１０mol％のオゾンを含む高純度酸素を基板に向けて射出させる。以降、圧力は5×10^{-6}To＊rrに調節する。そしてイオンビーム電流を増やして成膜を続ける。膜厚は成膜時間、成膜速度はイオンビーム電流またはイオンビーム加速電圧で調節する。

【００４１】本発明者が用いた装置での最適な成膜条件はつぎのとおりである。

ＣＳＺ：Ｗ成膜条件

成膜圧力	1×10^{-7}Torr以下（膜厚３ｎｍまで）
	5×10^{-6}Torr〔膜厚３ｎｍからO_2+O_3(１０mol％)導入〕
成膜温度	４５０℃（基板温度）
ターゲット	$CaO:ZrO_2:WO_3$＝１１：８０：９
イオン種	Ｘｅ
イオン源電圧	１５００Ｖ
イオン電流	９ｍＡ（膜厚３ｎｍまで）
	１４ｍＡ（膜厚３ｎｍから）

上記のようにして成膜し、膜厚が所望の値になったところで蒸着電源の出力を切り、O_2+O_3の導入を遮断して、基板を徐冷する。基板温度が十分低くなってから基板を蒸着槽から取出す。

【００４２】このようにして堆積したＣＳＺ：Ｗ膜の安定化剤と空孔消滅剤の濃度は実験精度の範囲内で同濃度（＝１５％）であった。また、膜の結晶構造はホタル石構造（立方晶）を有する単結晶エピタキシャル膜であった（詳細は後述する効果の項で説明）。本実施例４の製造方法は、前記実施例３の製造方法や後述の実施例と比較して、４５０℃という低温で成膜できる。これは高熱に耐えられない別の材料がＳｉ基体に形成されている場合などには、極めて有効であり、他の製造方法にない利点である。なお、詳細な説明はしないが、この製造方法を用いて（ただし条件は若干異なる）、第１の実施の形態（実施例１）に示した複合構造体の構造も実現できる。

【００４３】（５）複合構造体の製造方法の第３の実施の形態　<実施例５>

つぎに図１に記載した複合構造をレーザアブレーション法で実現する製造方法の実施例を説明する。まず、前記実施例１の製造方法と同様にＲＣＡ洗浄と希フッ酸洗浄とでＳｉ基板１の表面の汚染物および自然酸化物を除去する。

【００４４】つづいてＳｉ基板１上に酸化サマリウムSm_2O_3（サマリア）で安定化させ、酸化ニオビウムNb_2O_5で酸素イオン空孔を消滅化させた安定化ジルコニア膜２（以下ＳＳＺ：Ｎｂ）をレーザアブレーション法でＳｉ基板１に形成する。ターゲットはSm_2O_3粉末とZrO_2粉末とNb_2O_5粉末（いずれも９９．９９９％以上の純度）とをモル比でｘ：（１－ｘ－ｙ）：ｙに混合し、ホットプレスで円盤状（直径１０㎜、厚さ１０㎜）に整形したものである。ここでｘ＝約１８％、ｙ＝約１８％である。

【００４５】成膜の手順を説明すると、まず、成膜装置真空槽内のターゲットホルダにターゲットを設置し、前記洗浄直後のＳｉ基板１を蒸着槽中の基板ホルダに設置し、蒸着槽内を排気する。このホルダは基板を常温から６００℃までの温度に加熱する能力を有しており、ターゲットから約５ｃｍの距離を挟んで対抗している。蒸着装置の排気は強力であり、内部の圧力は10^{-9}Torr以下まで背圧を下げることが可能である。蒸着槽の圧力が10^{-6}Torrに達したら基板温度を加熱して所定の成膜温度にする。温度が安定し、かつ、蒸着槽内の圧力が10^{-8}Torr以下に下がったところでレーザ光源の出力をオンして高密度のレーザ光をタブレットに射突させ蒸着を開始する。本実施例のレーザ光源はＫｒＦ（波長２４８ｎｍ、パルス幅２０ｎｓ）エキシマレーザである。繰り返し周波数は１０Ｈｚ、エネルギー密度は１．３Ｊ／m^3であった。蒸着開始後、ＳＳＺの膜厚が３ｎｍになるまでは少なくとも10^{-8}Torr台の高真空を保って成膜する。そして３ｎｍを超えたところで外部から高純度酸素を導入し、圧力を5×10^{-5}Torrとする。標準的な成膜速度は１パルス当り０．０２５ｎｍであった。また、膜厚は成膜時間（パルス数と等価）で調節する。

【００４６】本発明者が用いた装置での最適な成膜条件はつぎのとおりである。

ＳＳＺ：Ｎｂ成膜条件

成膜圧力	1×10^{-7}Torr以下（膜厚３ｎｍまで）
	5×10^{-4}Torr（膜厚３ｎｍからO_2導入）
成膜温度	７７５℃（基板温度）
ターゲット	$Sm_2O_3:ZrO_2:Nb_2O_5$＝１８：６４：１８
ターゲット／基板距離	５ｃｍ
レーザ光源	ＫｒＦエキシマレーザ（エネルギー１３０ｍＪ）

励起パルス　幅２０ｎｓ、繰り返し周波数１０Ｈｚ

上記のようにして成膜し、膜厚が所望の値になったところでレーザ光源の発信を停止し、O_2の導入を止め、基板を徐冷する。基板温度が十分低くなってから基板を蒸着槽から取出す。

【００４７】このようにして堆積したＳＳＺ：Ｎｂ膜の安定化剤と空孔消滅剤の濃度は実験精度の範囲内で共に同濃度（＝１８％）であった。膜の結晶構造はホタル石構造（立方晶）を有する単結晶エピタキシャル膜であった。本製造方法で成膜した安定化ジルコニア膜の金属元素の組成は、蒸着条件の変更があってもターゲットの組成にほぼ等しくなるという特徴がある。これは安定化ジルコニア膜の組成が成膜装置に依存せずターゲットの組成で一義的に定まることを意味している。このような特徴は、実験成膜で得た最適条件を元にして大型の生産成膜装置を立ち上げる際に、最適化に要する時間を短縮できるという効果があり、有用である。なお、詳細な説明はしないが、この製造方法を用いて（ただし条件は若干異なる）、第２の実施の形態（実施例２）に示した複合構造体の構造も実現できる。

【００４８】（６）複合構造体の製造方法の第４の実施の形態　<実施例６>

つぎに図１に記載した複合構造を化学気相成長法（ＣＶＤ）で実現する製造方法の実施例を説明する。まず、前記実施例３の製造方法と同様に、ＲＣＡ洗浄と希フッ酸洗浄とでＳｉ基板１の表面の汚染物および自然酸化物を除去する。

【００４９】つづいてＳｉ基板１上に酸化サマリウムY_2O_3（イットリア）で安定化させ、酸化タンタルTa_2O_5で酸素イオン空孔を消滅させた安定化ジルコニア膜２（以下ＹＳＺ：Ｔａ）を減圧ＣＶＤ法でＳｉ基板１に形成する。原料はイットリウム・トリディピバロイルメタン：$Y(DPM)_3$、ジルコニウム・テトラディピバロイルメタン：$Zr(DPM)_4$、タンタル・ペンタエトキシド：$Ta(OC_2H_5)_5$、並びにO_2である。ここで、ＤＰＭは$C_{11}H_{19}O_2$を意味する。

【００５０】使用する装置は、図３に示すごとき伝統的なコールドウォール型の減圧ＣＶＤ装置である。この装置は、前記実施例３～５に示した物理的蒸着装置に比べて、装置の構造と操作法が複雑なので、図３を用いて詳しく説明する。図３において、１０は反応器である。反応器１０は、単結晶Ｓｉ基板１１を機械的に支持し所定の温度に保持するサセプタ１２と、蒸気を混合させ、混合させた蒸気をサセプタ１２に向けて均一に噴射させるシャワーヘッド１３と、堆積反応で生じた生成ガスや過剰な原料蒸気の排気口１４を備えている。１５、１６、１７はそれぞれ$Y(DPM)_3$原料、$Zr(DPM)_4$原料、$Ta(OC_2H_5)_5$原料の気化容器であり、温度調節機能を有している。気化容器１５、１６、１７には流量制御されたキャリアガス：Ａｒが導入され、気化された原料蒸気はこのＡｒガスによって輸送され、前記シャワーヘッド１３に導かれる。

【００５１】シャワーヘッド１３には、図のように、流量制御されたO_2もまた接続されている。気化容器１５、１６、１７とシャワーヘッド１３を結ぶ輸送管はそれぞれの原料気化容器の温度よりも約１０℃高い温度に保温されている。また、１８～２１は各原料蒸気の供給バルブである。反応器の生成ガスや過剰原料蒸気は、排気主バルブ２２を経由して、真空排気装置２３によって器外に排出される。また、２４は成膜中に反応器内の圧力を一定に保つための圧力調節器である。

【００５２】成膜の手順は次のとおりである。上記洗浄を終えたＳｉ単結晶基板１をサセプタ１２に乗せ、全ての原料蒸気供給バルブ１８～２１を閉じ、排気主バルブ２２を開けて反応器１０内を一旦真空にする。サセプタ１２の温度を所定の基板温度に設定すると共に、反応器１０の圧力を10^{-6}Torrまで減圧する。つづいて、圧力調節器２４を作動させると共に、供給バルブ１８～２１を開いて、各原料をシャワーヘッドから噴射させて成膜を開始する。

【００５３】本実施例における代表的な成膜条件を下に示す。

ＹＳＺ：Ｔａ成膜条件

成膜圧力	２Torr		
成膜温度	６５０℃（基板温度）		
原料、原料温度、流量	$Y(DPM)_3$、	１４０℃、	１５sccm
	$Zr(DPM)_4$、	１６５℃、	１７sccm
	$Ta(OC_2H_5)_5$、	１３０℃、	２０sccm
	O_2		２００sccm
シャワヘッドと基板間の距離	３ｃｍ		

上記のようにして成膜を行ない、膜厚が所望の値になったところで原料蒸気供給バルブ１８～２１を閉じ、圧力調節器２４を停止させ、反応器１０を真空排気しながら基板１１を徐冷する。基板温度が十分低くなってから基板１１を反応器１０から取出す。

【００５４】成膜で重要なのは、生成されたＹＳＺ：Ｔａ膜の組成、すなわち、安定化剤Y_2O_3と空孔消滅剤Ta_2O_5の濃度がほぼ等しく、所定の値５mol％～２５mol％の間に入るように、$Y(DPM)_3$原料と$Ta(OC_2H_5)_5$原料の温度と流量を制御するということである。

上記条件では安定化剤と空孔消滅剤の濃度が１１％程度であることが確かめられている。

【００５５】本製造方法で成膜した安定化ジルコニア膜は、前記物理的蒸着法で成膜したものに比べて、基板表面にある幾何学的な段差部などでも被覆性が極めて良好である。たとえば、アスペクト比（底辺長と壁長の比）が１：２の垂直溝構造基板に成膜すると、０．９以上の良好な被覆率（溝内部の最も薄い膜厚値と基板表面の膜厚値の比）が得られる。このような特徴は凹凸のある単結晶Ｓｉ基板に安定化ジルコニアを均一に成膜するような場合に非常に有利である。なお、詳細な説明はしないが、この製造方法を用いて（ただし条件は若干異なる）、第２の実施の形態（実施例２）に示した複合構造体の構造も実現できる。

【００５６】次に、図４は、上記の実施例３～６の製造方法で、Ｓｉ（１００）基板に作製した複合構造体の特性を示す図表である。安定化ジルコニア膜の厚みはすべて同じである。図４において、①は安定化ジルコニア膜の結晶性を示し、②はＭＩＳ容量の高周波Ｃ－Ｖ特性（のヒルテリシス）から抽出したイオンドリフト度：ΔＶ［Ｖ］を示す。なお、Ｃ－Ｖ特性の測定法は先述の従来技術の項において説明している。また、比較のため、図５を用いて説明した従来技術に基づく複合構造体の特性も併せて示した。

【００５７】図４に示すように、本発明に係る複合構造体の安定化ジルコニアの結晶系は全実施例とも立方晶系であり、完全にｃ軸配向している。そして格子定数は従来例の安定化ジルコニアのそれとほぼ等しい。また、単結晶Ｓｉ（１００）基板との結晶関係は、いずれもＳｉ（００１）‖ＸＳＺ：Ｙ（００１）、Ｓｉ［１１０］‖ＸＳＺ：Ｙ［１１０］である。ただし‖は平行を意味する。また、ＸＳＺ：Ｙは実施例３～６の製造方法による任意の安定化ジルコニア膜を表している。

【００５８】以上の結晶学的事実から、実施例３～６の製造方法で形成された安定化ジルコニア膜はすべて単結晶Ｓｉ基板にエピタキシャル成長しており、膜の結晶品＊
＊質は従来技術のよる安定化ジルコニア膜と比べて、なんら遜色ない膜であることが分かる。

【００５９】次に、イオンドリフトの目安であるＭＩＳ容量のΔＶに注目すると、従来例ではΔＶ＞５Ｖと甚だしく大きく、すでに述べたように、デバイス応用上、重大な障害になっていた。これに対し、図４の各実施例は全てΔＶ＜０．０５Ｖと２桁以上抑制されている。このΔＶから見積られる可動酸素イオンの濃度はNm＝２．９×１０^{10}／ｃｍ^{2}となり、ＭＯＳ集積回路のゲート酸化膜の可動イオン（ナトリウムなど）の濃度として許容される１０^{10}／ｃｍ^{2}台まで低減していることが理解される。

【００６０】こうして、実施例１および実施例２の複合構造体、および実施例３～実施例６の製造方法においては、安定化ジルコニア膜の結晶性を高品質に維持しながら、従来技術の問題点であった酸素イオン空孔によって引き起こされたイオンドリフト問題を解決することができる。

【００６１】次に、本発明は如何なるメカニズムでイオンドリフト問題を解決したかを説明する。イオンドリフトは安定化ジルコニアの酸素イオン空孔が電界で移動することによって引き起こされる。酸素イオン空孔ができるのは、従来技術の説明の項で述べたように、ジルコニアの４価のＺｒイオンが安定化剤に含まれる２価または３価の金属イオンに置換され、このとき、電気的中性条件を満足しなければならないからであった。しかしながら、本発明では安定化剤の添加と同時に５価または６価の金属イオンを含む酸素イオン空孔消滅剤を添加するので、酸素イオン空孔を生じさせることなく、電気的中性条件を満足させることができる。たとえば、ＹＳＺ：Ｔａの例（実施例１の構造と実施例３の製造方法）では、添加の様子を化学式で表すと下記（化３）式に示すようになる。

【００６２】

【化３】

$$\mathrm{YSZ:Ta}\qquad Y_2O_3 \xrightarrow{ZrO_2} 2\,\overset{-}{Y}(Zr) + \overset{++}{Vo} + 3\,Oo$$

…（化３）

$$Ta_2O_5 \xrightarrow{ZrO_2} 2\,\overset{+}{Ta}(Zr) + \overset{--}{Io} + 4\,Oo$$

【００６３】（化３）式において下の式はＴａ$_2$O$_5$を１mol添加すると、１molの過剰な格子間酸素イオンＩｏ$^{--}$が形成されることを意味するが、この格子間酸素イオンと、Ｙ$_2$O$_3$の空孔Vo^{++}とが、等量添加によって相殺しあうので、全体としては下記（化４）式に示すようになり、空孔が消滅する。

【００６４】

【化４】

ＹＳＺ：Ｔａ

$$Y_2O_3 + Ta_2O_5 \xrightarrow{ZrO_2} 2\overset{-}{Y}(Zr) + 2\overset{+}{Ta}(Zr) + 8O_O$$

…（化４）

【００６５】同様に、ＣＳＺ：Ｗの場合も全体的に下記（化５）式に示すようなり、酸素イオン空孔は生じない。

＊【００６６】

【化５】

＊

$$\text{CSZ:W} \quad CaO + WO_3 \xrightarrow{ZrO_2} \overset{--}{Ca}(Zr) + \overset{++}{W}(Zr) + 4O_O$$

…（化５）

【００６７】このように、本発明においては、可動電荷担体としての酸素イオン空孔が安定化ジルコニア膜内に存在しないので、複合構造体に電界が印加されてもイオンドリフトが起こらず、よってこの問題が解決できるのである。

【図面の簡単な説明】

【図１】本発明の複合構造体の第１の実施の形態（実施例１）を示す要部断面図。

【図２】本発明の複合構造体の第２の実施の形態（実施例２）を示す要部断面図。

【図３】本発明の製造方法の第４の実施の形態（実施例６）で使用する化学的気相成長装置の構成図。

【図４】本発明の各実施例と従来例との比較を示す図表。

【図５】従来技術による安定化ジルコニア／単結晶シリコン複合構造体のイオンドリフト現象を説明する実験結果を示す図。

【図６】イオンドリフトの機構を説明するための図。

【符号の説明】

１…単結晶Ｓｉ基板。

２…３価金属の酸化物からなる安定化剤と５価金属の酸化物からなる酸素イオン消滅剤を含有する単結晶安定化ジルコニア薄膜

２’…２価金属の酸化物からなる安定化剤と６価金属の酸化物からなる酸素イオン消滅剤を含有する単結晶安定化ジルコニア薄膜

１０…反応器 １１…単結晶Ｓｉ基板

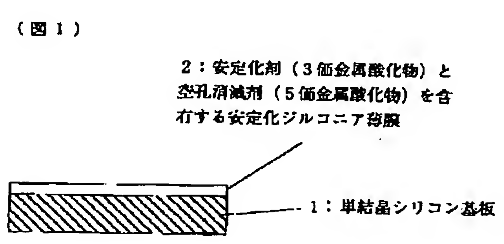
１２…サセプタ １３…シャワーヘッド

１４…排気口 １５、１６、１７…原料気化容器

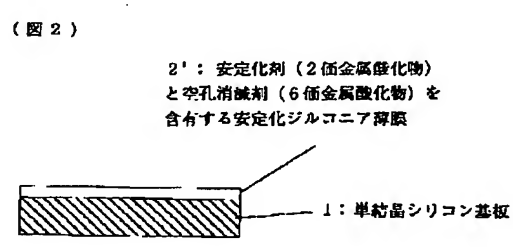
１８～２１…供給バルブ ２２…排気主バルブ

２３…真空排気装置 ２４…圧力調節器

【図１】

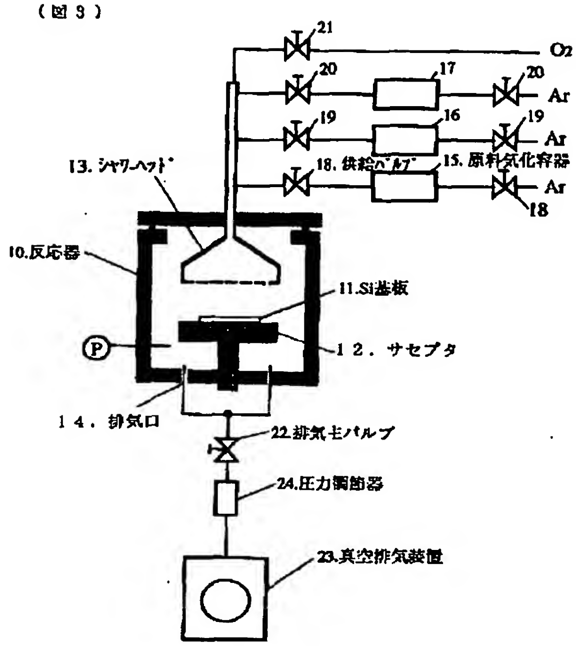


【図２】



【図３】

（図３）

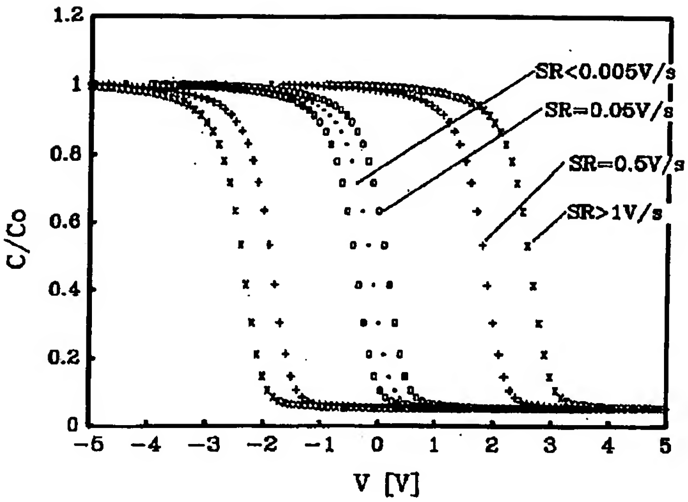


【図４】

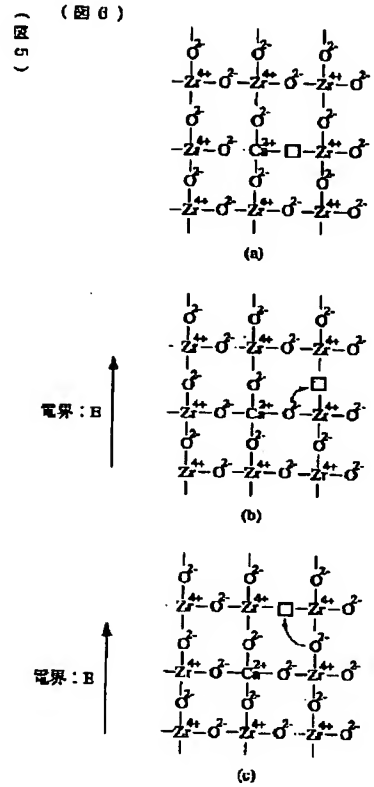
（図４）

	本発明の各実施例				
構造 製造方法	実施例１ 実施例３	実施例２ 実施例４	実施例１ 実施例５	実施例１ 実施例６	従来例
基板 薄膜	Si(100) YSZ: Ta	Si(100) CSZ: W	Si(100) SSZ: Nb	Si(100) YSZ: Ta	Si(100) YSZ
① ジルコニア 薄膜結晶性	a_0=0.51 nm Si(001)//YSZ(001) Si[110]//YSZ[110] 単結晶（立方晶）	a_0=0.52 nm Si(001)//CSZ(001) Si[110]//CSZ[110] 単結晶（立方晶）	a_0=0.51 nm Si(001)//SSZ(001) Si[110]//SSZ[110] 単結晶（立方晶）	a_0=0.51 nm Si(001)//YSZ(001) Si[110]//YSZ[110] 単結晶（立方晶）	a_0=0.52 nm Si(001)//YSZ(001) Si[110]//YSZ[110] 単結晶（立方晶）
② イオンドリフト度	0.01V以下	0.01V以下	0.01V以下	0.01V以下	～5V

【図5】



【図6】



* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] It is the membrane structure object characterized by providing the following, and a ferroelectric thin film is R1 (R1). At least one sort of rare earth elements chosen from Pr, Nd, Eu, Tb, Dy, Ho, Yb, Y, Sm, Gd, and Er, O is contained in Pb and Ti row and the rate of an atomic ratio is in the range of (Pb+R1)/Ti=0.8-1.3 and Pb/(Pb+R1) =0.5-0.99. The membrane structure object with which it has the perovskite type crystal structure, and is single (001) orientation, or orientation (001) and orientation (100) are intermingled. Substrate. The ferroelectric thin film formed on this substrate.
[Claim 2] The membrane structure object of a claim 1 with which the ferroelectric thin film is formed in the aforementioned front-face side of the substrate which has Si (100) side on a front face.
[Claim 3] It is the membrane structure object characterized by providing the following, the front face by the side of the ferroelectric thin film of a substrate has Si (100) side, and a ferroelectric thin film is R2 (R2). At least one sort of rare earth elements chosen from Pr, Nd, Eu, Tb, Dy, Ho, Yb, Y, Sm, Gd, Er, and La, O is contained in Pb and Ti row and the rate of an atomic ratio is in the range of (Pb+R2)/Ti=0.8-1.3 and Pb/(Pb+R2) =0.5-0.99. The membrane structure object with which it has the perovskite type crystal structure, and is single (001) orientation, or orientation (001) and orientation (100) are intermingled. Substrate. The ferroelectric thin film formed on this substrate.
[Claim 4] It is one membrane structure object of the claims 1-3 which it has an insulating ground thin film between a substrate and a ferroelectric thin film, and this insulating ground thin film has the perovskite crystal structure, are single (001) orientation when it is a tetragonal phase, and are single (100) orientation when it is a cubic.
[Claim 5] It is the membrane structure object of the claims 1-3 which it has a middle thin film between a substrate and a ferroelectric thin film, and this middle thin film makes a principal component the zirconium oxide by which this zirconium-oxide system thin film was stabilized by a zirconium oxide or rare earth elements (Sc and Y are included) including the zirconium-oxide system thin film, are single (001) orientation when it is a tetragonal phase or monoclinic system, and are single (100) orientation when it is a cubic.
[Claim 6] It is the membrane structure object of the claim 5 which this rare earth oxide system thin film exists [a middle thin film] between a zirconium-oxide system thin film and a ferroelectric thin film including a rare earth oxide system thin film, and this rare earth oxide system thin film makes a principal component the oxide of rare earth elements (Sc and Y are included), is single (001) orientation when it is a tetragonal phase or monoclinic system, and is single (100) orientation when it is a cubic.
[Claim 7] It is the membrane structure object of the claims 5 or 6 which it has an insulating ground thin film between a middle thin film and a ferroelectric thin film, and this insulating ground thin film has the perovskite crystal structure, are single (001) orientation when it is a tetragonal phase, and are single (100) orientation when it is a cubic.
[Claim 8] In contact with a ferroelectric thin film, it has a conductive ground thin film. this conductive ground thin film It is the conductive oxide thin film which consisted of oxides which have the oxide or the perovskite type crystal structure containing the conductive metal thin film which consisted of at least

one sort of Pt, Ir, Os, Re, Pd, Rh, and Ru, and/or In. It is one membrane structure object of the claims 1-7 which are single (001) orientation when it is a tetragonal phase, and are single (100) orientation when it is a cubic.
[Claim 9] One membrane structure object of the claims 1-8 whose ten-point averages of roughness height Rz with a criteria length of 500nm are 10nm or less in at least 80% of field of a ferroelectric thin film front face.
[Claim 10] One membrane structure object of the claims 1-9 with which below 60 atom % of Ti in a ferroelectric thin film is replaced by at least one sort of Zr, Nb, Ta, Hf, and Ce.
[Claim 11] The electron device which has one membrane structure object of the claims 1-10.
[Claim 12] The record medium which has one membrane structure object of the claims 1-10.
[Claim 13] The manufacture method of the ferroelectric thin film which performs vacuum evaporationo while facing the ferroelectric thin film which consists of an oxide which contains Pb and Ti at least forming on a substrate by plural vacuum depositions and introducing a oxidizing gas in a vacuum evaporationo reaction chamber at least, using a lead oxide and TiOx ($1<=x<=1.9$) as an evaporation source.
[Claim 14] It is the atomic ratio of the element supplied from an evaporation source Pb/Ti=E (Pb/Ti) It is an atomic ratio in the ferroelectric thin film which were formed by carrying out Pb/Ti=F (Pb/Ti) The manufacture method of the ferroelectric thin film of a claim 13 set to E (Pb/Ti)/F (Pb/Ti) =1.5-3.5 when it carries out.
[Claim 15] The manufacture method of the ferroelectric thin film of claims 13 or 14 using the oxygen which at least the part radical-ized as a oxidizing gas.
[Claim 16] The manufacture method of one ferroelectric thin film of the claims 13-15 which make temperature of a substrate 500-700 degrees C, and perform vacuum evaporationo.
[Claim 17] The manufacture method of one ferroelectric thin film of the claims 13-16 that the ferroelectric thin film containing at least one sort of Zr, Nb, Ta, Hf, and Ce is formed.
[Claim 18] The manufacture method of one ferroelectric thin film of the claims 13-17 applied to manufacture of one membrane structure object of the claims 1-10.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the membrane structure object containing a ferroelectric thin film, the electron device equipped with this membrane structure object, the record medium using this membrane structure object, and the method of manufacturing a ferroelectric thin film by plural vacuum depositions. The aforementioned membrane structure object is applied to the record medium which is made to carry out polarization reversal of the ferroelectric with various electron devices, such as non-volatile memory which built the ferroelectric into the semiconductor device, an infrared sensor, an optical modulator, an optical switch, and OEIC (opto-electronic integrated circuit : opto-electronic integrated circuits), or an AFM (atomic force microscope) probe, and records information.
[0002]
[Description of the Prior Art] The electron device which formed the dielectric thin film on Si substrate which is a semiconducting-crystal substrate, and was integrated is devised. The dielectric separation LSI by still higher LSI of a degree of integration and SOI technology is considered by by combining a semiconductor and a dielectric. Moreover, the ferroelectric which is a kind of a dielectric is applicable to non-volatile memory by using polarization reversal, and since an infrared sensor, an optical modulator, optical-switch OEIC, etc. can be constituted, examination of a ferroelectric thin film material is advanced energetically. Moreover, application to the record medium with which a ferroelectric thin film records information using the polarization reversal by the AFM probe etc. is also considered. In the non-volatile memory and the record medium using polarization reversal of a ferroelectric, as a ferroelectric thin film material, a remanence value is large and what bears the repeat of record and read-out is needed.

[0003] Although the memory of the structure which used the ferroelectric for the gate of FET is devised as one sort of non-volatile memory, the memory which uses a ferroelectric for the gate has plentifully the point which should problem-etc.-solve the problem on production, and ferroelectric physical properties of thin film, and has not resulted in utilization as stated to electronic-intelligence communication society issue Shingaku Giho, SDM 93-136, ICD 93-130, (1993-11), and 53 pages. By this type of memory, although it is ideal to make a memory cell into metal-ferroelectric-semiconductor (MFS) structure, since realization is difficult, generally it considers as metal-ferroelectric-insulator-semiconductor (MFIS) structure or metal-ferroelectric-metal-insulator-semiconductor (MFMIS) structure. In such structures, in order to carry out polarization reversal of the ferroelectric and to carry out memory operation, you have to apply the electric field of sufficient intensity for a ferroelectric. With MFIS structure and MFMIS structure, since a ferroelectric and an insulator become equivalent to the series connection of a capacitor, in order to apply electric field to a ferroelectric enough, the device which lowers the dielectric constant of a ferroelectric and gathers the dielectric constant of an insulator is needed.
[0004] as the material of a present and ferroelectric thin film -- lead system oxides, such as $PbTiO_3$,

PZT (PbZrO3-PbTiO3 system), and PLZT (PbZrO3-PbTiO3 system by which La 2O3 was added), and Bi2 Ti2 NbO9 etc. -- it inquires by the polarization property excellent in Bi system oxide being shown

[0005] However, since a dielectric constant will become high about with 1000 if it thin-film-izes, when it uses as a ferroelectric thin film in the above-mentioned MFIS structure and above-mentioned MFMIS structure, it is difficult for PZT or PLZT to impress sufficient voltage.

[0006] On the other hand, it is PbTiO3. The dielectric constant in bulk is as small as about [100 or less] at a room temperature, and spontaneous polarization is 80microC/cm2 at the theoretical value of a bulk crystal. Compared with the material of other composition, a big value is shown wonderfully, and the Curie point is as high as 500 degrees C. That is, the most ideal value is indicated by the collection of data when thinking as a ferroelectric material of a memory use. Moreover, PbTiO3 Even when it thin-film-izes, a dielectric constant is about 500 and a low. However, PbTiO3 Various troubles are becoming clear as a result of furthering the research and development which thin-film-ize and are made into an electron device. the voltage Ec which carries out polarization reversal in the first place -- 85 kV/cm the defatigation property by polarization reversal, i.e., a repeat property, being bad to that leak arises in a thin film by being too high, the second crystal defect, semiconductor-ization, etc., and the third, and deteriorating in about 1000 times -- it comes out

[0007] In order to acquire a ferroelectric property, it is necessary to make it crystallize in the thin film material of the above-mentioned lead system oxide or Bi system oxide. the method of heating the temperature under thin film formation at 600 degrees C or more in order to make it crystallizing, and the method of annealing above 600 degrees C after membrane formation -- Jpn.J.Appl.Phys. -- 31, 3029 (1992), and Jpn.J.Appl.Phys. -- 33, 5244 (1994), and Mat.Res.Soc.Sympo.Proc. -- it is indicated by 243, 473 (1993), etc. However, Pb and Bi have high vapor pressure also in any of a metal and an oxide, and in order that they may evaporate in hot heat treatment and may cause a composition gap, a difficulty is in composition control.

[0008] Generally, in order to secure the device property optimal as a ferroelectric material, and its repeatability, it is desirable to use a single crystal. In the polycrystalline substance, it is difficult to obtain a good device property because of the disturbance of the physical quantity by the grain boundary. This is the same also about a thin film material, and a ferroelectric epitaxial film near the most perfect possible single crystal is desired. The same is said of the ferroelectric thin film in the non-volatile memory of the above-mentioned MFIS structure or MFMIS structure, and to be a dielectric epitaxial film near the most perfect possible single crystal is desired. Moreover, also in the medium (usually MFIS structure or MFMIS structure) which records using probes, such as AFM and STM, since the writing of a high-density bit will be attained if the ferroelectric epitaxial film near the most perfect possible single crystal is used, the realization is desired. Although it is necessary to grow epitaxially a metal thin film and a ferroelectric thin film on Si substrate which is a semiconductor substrate in order to realize a ferroelectric epitaxial film with MFIS structure or MFMIS structure, now, it does not realize yet.

[0009] With the ferroelectric material of a lead system, there is no composition gap and the thin film more near a single crystal is not obtained on the semiconductor substrate until now. Moreover, the ferroelectric material of a lead system of reactivity with Si used as a substrate will also be high, and it will have serious influence for the integrated-circuit property produced in Si substrate by diffusion of Pb to Si substrate.

[0010]

[Problem(s) to be Solved by the Invention] this invention is made in order to conquer the trouble mentioned above. The purpose of this invention is offering the membrane structure object which has a ferroelectric thin film with little degradation, even if a dielectric constant is comparatively low, a remanence is large, and a polarization turn over voltage is low and repeats polarization reversal. Moreover, other purposes of this invention have the fixed composition which was impossible until now, and are offering the method a crystalline high lead system ferroelectric thin film's being manufactured.

[0011]

[Means for Solving the Problem] The above-mentioned purpose is attained by one composition of

following the (1) - (18).
(1) It is the membrane structure object which has a substrate and the ferroelectric thin film formed on this substrate, and a ferroelectric thin film is R1 (R1). At least one sort of rare earth elements chosen from Pr, Nd, Eu, Tb, Dy, Ho, Yb, Y, Sm, Gd, and Er, O is contained in Pb and Ti row and the rate of an atomic ratio is in the range of (Pb+R1)/Ti=0.8-1.3 and Pb/(Pb+R1) =0.5-0.99. The membrane structure object with which it has the perovskite type crystal structure, and is single (001) orientation, or orientation (001) and orientation (100) are intermingled.
(2) The membrane structure object of the above (1) with which the ferroelectric thin film is formed in the aforementioned front-face side of the substrate which has Si (100) side on a front face.
(3) It is the membrane structure object which has a substrate and the ferroelectric thin film formed on this substrate, the front face by the side of the ferroelectric thin film of a substrate has Si (100) side, and a ferroelectric thin film is R2 (R2). At least one sort of rare earth elements chosen from Pr, Nd, Eu, Tb, Dy, Ho, Yb, Y, Sm, Gd, Er, and La, O is contained in Pb and Ti row and the rate of an atomic ratio is in the range of (Pb+R2)/Ti=0.8-1.3 and Pb/(Pb+R2) =0.5-0.99. The membrane structure object with which it has the perovskite type crystal structure, and is single (001) orientation, or orientation (001) and orientation (100) are intermingled.
(4) It is one membrane structure object of above-mentioned (1) - (3) which it has an insulating ground thin film between a substrate and a ferroelectric thin film, and this insulating ground thin film has the perovskite crystal structure, is single (001) orientation when it is a tetragonal phase, and is single (100) orientation when it is a cubic.
(5) It is the membrane structure object of above-mentioned (1) - (3) which is single (100) orientation when it has a middle thin film and this middle thin film makes a principal component the zirconium oxide by which this zirconium-oxide system thin film was stabilized by a zirconium oxide or rare earth elements (Sc and Y are included) including the zirconium-oxide system thin film, and it is single (001) orientation when it is a tetragonal phase or monoclinic system and it is a cubic, while a substrate and a ferroelectric thin film.
(6) It is the membrane structure object of the above (5) which this rare earth oxide system thin film exists [a middle thin film] between a zirconium-oxide system thin film and a ferroelectric thin film including a rare earth oxide system thin film, and this rare earth oxide system thin film makes a principal component the oxide of rare earth elements (Sc and Y are included), is single (001) orientation when it is a tetragonal phase or monoclinic system, and is single (100) orientation when it is a cubic.
(7) It is the above (5) or the membrane structure object of (6) which it has an insulating ground thin film between a middle thin film and a ferroelectric thin film, and this insulating ground thin film has the perovskite crystal structure, is single (001) orientation when it is a tetragonal phase, and is single (100) orientation when it is a cubic.
In contact with a ferroelectric thin film, it has a conductive ground thin film. (8) This conductive ground thin film It is the conductive oxide thin film which consisted of oxides which have the oxide or the perovskite type crystal structure containing the conductive metal thin film which consisted of at least one sort of Pt, Ir, Os, Re, Pd, Rh, and Ru, and/or In. It is one membrane structure object of above-mentioned (1) - (7) which is single (001) orientation when it is a tetragonal phase, and is single (100) orientation when it is a cubic.
(9) a ferroelectric -- a thin film -- a front face -- at least -- 80 -- % -- a field -- setting -- criteria -- length -- 500 -- nm -- ten -- a point -- the average of roughness height -- Rz -- ten -- nm -- less than -- it is -- the above -- (-- one --) - (-- eight --) -- either -- a membrane structure -- the body .
(10) One membrane structure object of above-mentioned (1) - (9) with which below 60 atom % of Ti in a ferroelectric thin film is replaced by at least one sort of Zr, Nb, Ta, Hf, and Ce.
(11) The above (1) Electron device which has one membrane structure object of - (10).
(12) The above (1) Record medium which has one membrane structure object of - (10).
(13) The manufacture method of the ferroelectric thin film which performs vacuum evaporationo while facing the ferroelectric thin film which consists of an oxide which contains Pb and Ti at least forming on a substrate by plural vacuum depositions and introducing a oxidizing gas in a vacuum evaporationo

reaction chamber at least, using a lead oxide and TiOx (1<=x<=1.9) as an evaporation source.
(14) It is the atomic ratio of the element supplied from an evaporation source Pb/Ti=E (Pb/Ti) It is an atomic ratio in the ferroelectric thin film which were formed by carrying out Pb/Ti=F (Pb/Ti) The manufacture method of the ferroelectric thin film the above (13) set to E (Pb/Ti)/F (Pb/Ti) =1.5-3.5 when it carries out.
(15) The above (13) using the oxygen which at least the part radical-ized as a oxidizing gas, or the manufacture method of the ferroelectric thin film of (14).
(16) The manufacture method of one ferroelectric thin film of above-mentioned (13) - (15) which makes temperature of a substrate 500-700 degrees C, and performs vacuum evaporationo.
(17) The manufacture method of one ferroelectric thin film of above-mentioned (13) - (16) that the ferroelectric thin film containing at least one sort of Zr, Nb, Ta, Hf, and Ce is formed.
(18) The manufacture method of one ferroelectric thin film of above-mentioned (1) above-mentioned [which is applied to manufacture of one membrane structure object of - (10)] (13) - (17).
[0012]
[Function of the Invention] At this invention, it is PbTiO3 as composition of a ferroelectric thin film. What added predetermined rare earth elements is used for system composition. PbTiO3 Although spontaneous polarization, a dielectric constant, and the Curie point are suitable for memory, there are troubles, like that the voltage Ec which carries out polarization reversal is too high, that leak arises in a thin film, and the defatigation property by polarization reversal is bad. The above trouble was solved by this invention.
[0013] In this invention, they are rare earth elements at a predetermined ratio PbTiO3 By adding, Ec was reduced and, moreover, it made it possible to suppress reduction of the remanence value Pr accompanying it. Moreover, this invention persons investigated in detail the rare earth elements which are hard to produce semiconductor-ization, and realized the ferroelectric thin film with little leak. It traced having influenced the defatigation property of polarization reversal of the kind and amount of rare earth elements to add simultaneously, and the ferroelectric thin film which was excellent in the repeat property was realized.
[0014] Specifically, in this invention, Pb, Ti, and O are contained as a ferroelectric thin film, and it is the above R2 at the above R1 and the second mode in the first mode further. What is contained is used. In the second mode, La is increasing as alternative of rare earth elements to the first mode.
[0015] The ferroelectric thin film in the first mode is single (001) orientation, or orientation (001) and orientation (100) are intermingled. Since it has such orientation, the property as a ferroelectric thin film becomes good, especially leak decreases.
[0016] In addition, adding Sc, Y, run TANOINDO, etc. like the first mode into the oxide ferroelectric material containing Pb and Ti is indicated by JP,7-94608,A. In the example of this official report, the ferroelectric thin film is formed by the spatter on Si (110) substrate. In a spatter target, it is Y2 O3. Included PbTiO3 It uses. In this official report, since the ferroelectric thin film is formed by such method, the above-mentioned orientation in the first mode is not realized, but it is thought that it is in the state near a polycrystal film. A remanence value will become small if crystallinity is bad. In the example of this official report, it is making to suppress reduction of the remanence value by the repeat of defatigation by polarization reversal, i.e., polarization reversal, into the effect. However, since it has the small remanence value that defatigation by polarization reversal becomes small in this official report, it is thought that it originates in the stress produced by polarization reversal having become small. Though the above-mentioned defatigation is suppressed when a remanence value is small, it cannot be said that it is practical.
[0017] Moreover, the ferroelectric material of the lead-titanate system which added Sm or Gd used in the first mode is indicated by JP,7-202039,A. In this official report, the laminating of a titanium-nitride layer and the platinum layer was turned up, and the ferroelectric layer is formed. As the formation method of a ferroelectric layer, a spatter, CVD, the sol-gel method, and the laser abrasion method are mentioned, and the sol-gel method is explained as an example. When multilayer structure and the formation method given [this] in an official report are used, the ferroelectric thin film of the above-

mentioned orientation in the first mode cannot be formed, and, naturally the effect in the first mode is not realized, either.

[0018] Moreover, the ferroelectric material of the titanic-acid lead zirconate system which added Er used in the first mode is indicated by JP,7-73732,A. However, in this official report, the sol-gel method is mentioned as the formation method of a ferroelectric thin film. In a sol-gel method, the ferroelectric thin film of the above-mentioned orientation in the first mode cannot be formed, and, naturally the effect in the first mode is not realized, either.

[0019] In the second mode, the front face by the side of a ferroelectric thin film uses what has Si (100) side as a substrate in which a ferroelectric thin film is formed. According to the experiment of this invention persons, it is TiO (Pb, La)3. Although there is no leak and the polarization turn over voltage Ec becomes low when a thin film is formed on Si (100) substrate, when it forms, for example on a MgO (100) substrate, there will be much leak and Ec will become high. For this reason, Si (100) substrate is used in the second mode. Moreover, there is also a merit which is mentioned later in Si substrate.

[0020] The ferroelectric thin film of a lead-titanate system or a titanic-acid lead zirconate system which added La used in the second mode is indicated by JP,59-138004,A, a 60-172103 official report, a 62-252005 official report, a 62-252006 official report, a 4-199745 official report, JP,3-35249,B, etc.

[0021] Although some in which orientation (001) and orientation (100) were intermingled are in the ferroelectric thin film indicated by these official reports, there is nothing that could form such an orientation film on Si (100) substrate like the second mode, and it uses the MgO (100) substrate altogether. Although the above-mentioned orientation can be attained comparatively easily if a MgO (100) substrate is used, since the coefficient of thermal expansion is larger than Si, in case it is cooled to a room temperature after formation, big stress will arise in a ferroelectric thin film, and, thereby, the leak of MgO will increase remarkably. In addition, it is thought that it is because it is observed as it is easy to be extended in the direction where the crystal lattice of a ferroelectric thin film is perpendicular to a substrate side in order it has a large substrate that the above-mentioned orientation can be attained comparatively easily [when a MgO (100) substrate is used] and to contract, and c axis is carrying out orientation at right angles to a substrate side seemingly for this reason. When a ferroelectric thin film with a thickness of about 300nm is formed on a MgO substrate and the property is actually measured, compared with the amount of preferred orientation presumed from an X diffraction etc., only a low property is acquired remarkably but there is much especially leak remarkably. As for this, it is presumed to be the cause by contraction of a MgO substrate that a lot of residual stress in a ferroelectric thin film is accumulated.

[0022] Among the above-mentioned official reports, by JP,4-199745,A, as shown in the X diffraction view of a view 2, La addition lead-titanate thin film is formed on Si (100) substrate. However, in this thin film, only the peak by each side of (100), (110), and (111) is accepted, and it has not become orientation (001) so that clearly from a view 2. Although there was nothing that has formed La addition lead-titanate thin film of orientation (001) on Si (100) substrate conventionally, this is clear also from the publication of this official report.

[0023] Since the vapor pressure of Pb is high as compared with other elements when thin-film-izing the dielectric materials of Pb system, it is easy to cause a composition gap, and control of the amount of Pb (s) is difficult. With the ferroelectric material of Pb system, there is no composition gap and the thin film more near a single crystal is not obtained on the semiconductor substrate until now. In this invention, this property of Pb was used conversely and the optimum conditions of plural vacuum depositions were found out. On this condition, Pb is incorporated by the self-adjustment target the neither more nor less at a perovskite crystal, and the target ferroelectric crystal is obtained. Therefore, according to the manufacture method of this invention, crystalline high Pb system ferroelectric thin film is obtained, and, for this reason, outstanding strong dielectric characteristics are realized. Furthermore, on Si substrate, epitaxial growth becomes possible and it is very effective on electron device application. Moreover, PbTiO3 Since it is considering as the foundations of composition and a dielectric constant becomes comparatively low, it is suitable for memory application of the structure which used the ferroelectric for the gate of FET. The thin film optimal as an object for memory which applied MFIS structure and

MFMIS structure especially is obtained.
[0024]
[Embodiments of the Invention] The membrane structure object of this invention has at least a substrate and the ferroelectric thin film formed on this substrate. It is desirable that a middle thin film or an insulating ground thin film is prepared between a substrate and a ferroelectric thin film, and it is more desirable that the laminating is carried out in the order of a substrate, a middle thin film, an insulating ground thin film, and a ferroelectric thin film. Moreover, when preparing a conductive ground thin film, a conductive ground thin film is prepared in contact with a ferroelectric thin film. In this case, it is desirable that a middle thin film or an insulating ground thin film is prepared between a substrate and a conductive ground thin film, and it is more desirable that the laminating is carried out in the order of a substrate, a middle thin film, an insulating ground thin film, a conductive ground thin film, and a ferroelectric thin film. Hereafter, the manufacture method is explained to each thin film and a substrate row in detail.
[0025] Composition of the ferroelectric thin film which the membrane structure object of a <ferroelectric thin film> this invention has is PbTiO3. Rare earth elements R1 predetermined to system composition Or R2 It adds. The following and R1 And R2 Rn It names generically.
[0026] Rn PbTiO3 It replaces by Pb located in A site of the basic perovskite which consists of material, and a crystal is made to transform. PbTiO3 A-axis: 3.904A and c axis:4.152A It is a tetragonal phase type perovskite structure, and has a polarization shaft in c shaft orientations. Since this crystal deformation decreases the ratio of an a-axis and c axis, although it decreases spontaneous polarization slightly, it can reduce the voltage (Ec) needed for the polarization reversal which poses a problem. On the other hand, it is Rn. It is PbTiO3 in the rare earth elements of an except, for example, Ce. Since it replaces by the element located in B site, and a crystal cannot be transformed effectively and spontaneous polarization falls extremely, it is not desirable to device application.
[0027] The ratios of the element in a ferroelectric thin film are (Pb+Rn)/Ti=0.8-1.3 and Pb/(Pb+Rn) =0.5-0.99, and are /(Pb+Rn) Ti=0.9-1.2 and Pb/(Pb+Rn) =0.7-0.97 preferably. When (Pb+Rn)/Ti is too small, it becomes impossible to desire a crystalline improvement effect, and if (Pb+Rn)/Ti is too large, formation of a homogeneous thin film will become difficult. Moreover, good dielectric characteristics are obtained by making (Pb+Rn)/Ti into the above-mentioned range. If Pb/(Pb+Rn) is too small, while spontaneous polarization will become small, a dielectric constant will also become large or more with 1000. On the other hand, if Pb/(Pb+Rn) is too large, the addition effect of rare earth elements, i.e., the fall effect of Ec, will become inadequate. It is easily realizable by controlling to mention the formation conditions of a ferroelectric thin film later to make Pb/(Pb+Rn) into the above-mentioned range. Pb, Ti, and Rn It can ask for content by the X-ray fluorescence analysis.
[0028] A lead titanate is Rn added in this invention although it is generally Pb:Ti:O=1:1:3. The ratio of oxygen changes with a kind and amounts, and it is usually 2.7 to about 3.3.
[0029] As for a ferroelectric thin film, it is desirable to have the perovskite crystal structure and to have orientation at least (001). (001) PbTiO3 in which <001> shafts are perpendicular to the field inboard of a ferroelectric thin film, and have the crystal structure of a perovskite system in orientation Since the ferroelectricity of system material is acquired with <001> shafts, it is more desirable that a field (001) is a single (001) orientation film parallel in a film surface, and it is still more desirable that it is the epitaxial film defined in this specification. However, in this invention, orientation (100) with a field (100) parallel in a film surface may be intermingled. (100) Although an orientation crystal may form 90-degree domain and decreases spontaneous polarization slightly in this case, it does not become a serious obstacle. Moreover, since the stress in a thin film is decreased when 90-degree domain is formed, it is sometimes effective for improvement in a ferroelectric property. As for the peak intensity ratio in an X diffraction, it is usually desirable that (100)/(001) is three or less. In addition, even when orientation (100) is intermingled, it is desirable that it is the epitaxial film defined in this specification.
[0030] The desirable crystallographic-axis orientation relationship of the ferroelectric thin film in the case of using Si (100) substrate and Si substrate is as follows. In addition, Si is a cubic. When the ferroelectric thin film of a perovskite structure is single (001) orientation, they are perovskite [100]// Si

[010]. Moreover, when orientation (001) and orientation (100) are intermingled, ferroelectric thin films are perovskite [100]// Si [010] about a perovskite (001) orientation crystal, and are perovskite [001]// Si [010] about a perovskite (100) orientation crystal. That is, as for a ferroelectric thin film and Si substrate, it is desirable that the shafts which exist in a field are parallel.

[0031] In addition, the single orientation film in this specification means the thing of the crystallization film with which the target crystal face is equal to a substrate front face and parallel. concrete -- for example, a single (001) orientation film, i.e., a c-th page single orientation film, -- 10% or less of the maximum peak intensity of the field (00L) reflection of reflectivity other than a field (00L) by membranous 2 theta-theta X diffraction (XRD) -- desirable -- 5% or less of thing -- it is . in addition, this specification -- setting (00L) -- etc. (002) etc. -- the display which names an equivalent field generically -- it is -- etc. (L00) etc. -- ******** -- it is the same (001)

[0032] Moreover, when an epitaxial film makes the inside of a film surface a X-Y side and sets the Z-axis as the direction of thickness in this specification, the crystal is gathering and carrying out orientation to both the X-axis, a Y-axis, and Z shaft orientations. 10% or less of the maximum peak intensity of the field which the peak intensity of reflection of things other than the field made into the purpose specifically makes the purpose when measurement by the X diffraction is performed in the first place -- desirable -- 5% or less -- it is necessary to be . an epitaxial film (001), i.e., a c-th page epitaxial film, -- membranous 2 theta-theta X diffraction -- peak intensity other than a field (00L) -- 10% or less of the maximum peak intensity of a field (00L) -- desirable -- 5% or less -- it is . RHEED evaluation needs to show a spot or a streak pattern to the second. It can be called an epitaxial film if these conditions are satisfied. In addition, RHEED is a reflective high-speed electron diffraction (Reflction High Energy Electron Diffraction), and RHEED evaluation is the index of the orientation of the crystallographic axis in a film surface.

[0033] Although a part of Ti in a ferroelectric thin film may be replaced by at least one sort of Zr, Nb, Ta, Hf, and Ce, as for the substitutional rate of Ti by these elements, it is desirable that it is below 60 atom %. When a substitutional rate is too high, antiferroelectricity may be shown without becoming a ferroelectric. In addition, when Ti is replaced and above-mentioned /(Pb+Rn) Ti is computed, these substitution elements are converted into Ti and considered.

[0034] Although especially the material of the substrate used by the <substrate> this invention is not limited, a single crystal is used preferably. Specifically, although any, such as semiconductors, such as insulators, such as a magnesia, a strontium titanate, sapphire, a zirconia, a stabilized zirconia, a lithium niobate, and a lithium tantalate, and gallium arsenide, silicon, may be used, Si single crystal is used preferably. When it uses so that the field (100) of Si single crystal may turn into a substrate front face especially, the ferroelectric thin film which was excellent in the property can be formed. Moreover, since it is used widely by the semiconductor device, when composite-izing the membrane structure object of this invention with other elements, it is suitable, and since the coefficient-of-thermal-expansion coefficient of Si corresponds even when using it combining other elements, it is desirable. For example, since 1 figure of coefficients of thermal expansion of a MgO substrate differs from Si, they are unsuitable for such a use. Moreover, Si is comparatively cheap.

[0035] It is desirable to prepare an insulating ground thin film between a <insulating ground thin film> substrate and a ferroelectric thin film. In not preparing the conductive ground thin film mentioned later, an insulating ground thin film usually exists in contact with a ferroelectric thin film.

[0036] An insulating ground thin film has the perovskite crystal structure. A perovskite type structure is a chemical formula ABO3. It is expressed. Here, A and B express a cation respectively. One or more sorts chosen from calcium, Ba, Sr, Pb, K, Na, Li, La, and Cd as A in this invention, especially Ba or Sr is desirable, and one or more sorts chosen from Ti, Zr, Ta, and Nb as B, especially Ti are desirable. That is, as for an insulating ground thin film, in this invention, it is desirable to form a barium titanate or a strontium titanate as a principal component.

[0037] atomic-ratio A/B in such a perovskite type compound -- desirable -- 0.8-1.3 -- it is 0.9-1.2 more preferably Less than by 0.8, if it becomes impossible to desire an improvement effect of crystallinity [A/B] and A/B exceeds 1.3, formation of a homogeneous thin film will become difficult. It can ask for

the composition ratio of A/B from an X-ray fluorescence analysis. ABO3 Composition of O which can be set is not limited to 3. Since there are some which construct the perovskite structure stabilized in an oxygen defect or hyperoxia depending on perovskite material, it is ABOX. It sets and, as for the value of x, it is desirable that it is 2.7-3.3.

[0038] It is desirable that the c-th page carries out orientation to single (001) orientation, i.e., a substrate front face, and parallel individually when it is a tetragonal phase, and when it is a cubic, it is desirable that the a-th page carries out orientation to single (100) orientation, i.e., a substrate front face, and parallel individually, and even when it is any, it is more desirable [an insulating ground thin film] that it is an epitaxial film. Moreover, as for the orientation relationship of an insulating ground thin film and Si (100) substrate, it is desirable that they are tetragonal [100]// Si [010], or cubic [010]//Si [010]. That is, as for a thin film and a substrate, it is desirable that shafts are parallel in a field. Such a laminated structure is effective for raising the crystallinity of the conductive ground thin film further formed on this structure, or a ferroelectric thin film, and forming these as a single orientation film or an epitaxial film. Since an insulating ground thin film has good grid adjustment with a ferroelectric thin film, a crystalline high ferroelectric thin film is obtained.

[0039] An insulating ground thin film functions also as an insulator in MFIS structure or MFMIS structure.

[0040] The conductive ground thin film prepared by sticking to a ferroelectric thin film between a <conductive ground thin film> substrate and a ferroelectric thin film functions as a lower electrode for constituting MFMIS structure required for the electrode for ferroelectric thin films, and memory application of a ferroelectric thin film.

[0041] Although it is desirable to consist of metals as for a conductive ground thin film, you may be the oxide and the conductive perovskite oxide containing In, and it is good also as composition which carried out the laminating of a metal membrane and the oxide film. As a metal, the metal simple substance and alloy containing at least one sort of Pt, Ir, Os, Re, Pd, Rh, and Ru are desirable. As the oxide containing In, or a conductive perovskite oxide, In 2O3, In 2O3 (Sn dope), CoO (R, Sr)3, RuO (R, Sr, calcium)3, RuO (R, Sr)3, SrRuO3, MnO(s) (R, Sr)3, or these related compounds are desirable, for example. In addition, in the aforementioned compound, R is the rare earth elements containing Sc and Y.

[0042] Like an insulating ground thin film, when it is a tetragonal phase and they are single (001) orientation and a cubic, it is desirable that it is single (100) orientation, and even when it is any, as for a conductive ground thin film, it is more desirable that it is an epitaxial film. Moreover, as for the orientation relationship of a conductive ground thin film and Si (100) substrate, it is desirable that they are tetragonal [100]// Si [010], or cubic [010]//Si [010]. That is, as for a thin film and a substrate, it is desirable that shafts are parallel in a field. Such a laminated structure is effective for raising the crystallinity of the ferroelectric thin film further formed on this structure, and forming as a single orientation film or an epitaxial film. Since a conductive ground thin film has good grid adjustment with a ferroelectric thin film, a crystalline high ferroelectric thin film is obtained.

[0043] As for a conductive ground thin film, it is desirable that the specific resistance in bulk is 10-5 - 10-2ohmcm. Moreover, as for the specific resistance as a thin film, it is desirable that they are 10-5 - 10-2ohmcm. Moreover, the conductive ground thin film may consist of superconducting materials.

[0044] It is desirable that a middle thin film is prepared between a <middle thin film> substrate and a ferroelectric thin film. When preparing an insulating ground thin film, an insulating ground thin film will be located between a middle thin film and a ferroelectric thin film. A middle thin film consists of zirconium-oxide system thin films, or consists of this and a rare earth oxide system thin film. In addition, a rare earth oxide system thin film is prepared between a zirconium-oxide system thin film and a ferroelectric thin film. A middle thin film functions as an insulator in MFMIS structure or MFIS structure.

[0045] A zirconium-oxide system thin film zirconium-oxide system thin film makes a principal component the zirconium oxide (stabilized zirconia) which made the zirconium oxide the principal component or was stabilized by rare earth elements (Sc and Y are included). By preparing this thin film,

ablation of the ground thin film prepared on it or a ferroelectric thin film can be prevented. Moreover, since this thin film has good grid adjustment with the ground thin film which consists of a barium titanate etc., a crystalline high ferroelectric thin film is obtained as a result.
[0046] A zirconium oxide and a stabilized zirconia have the desirable thing of the composition expressed with Zr1-x Rx O2-delta (R is the rare earth elements containing Sc and Y, and is x= 0 to 0.75, and delta=0-0.5). About x and delta, it mentions later. It is desirable that it is at least one sort chosen from Pr, Ce, Nd, Gd, Tb, Dy, Ho, and Er as R.
[0047] As for a zirconium-oxide system thin film, it is desirable to have single crystal orientation. Since a grain boundary exists in the thin film which has two or more crystal faces, this is because epitaxial growth of the ground thin film on it or a ferroelectric thin film becomes impossible. Specifically, when it is a tetragonal phase or monoclinic system and is single (001) orientation and a cubic, it is desirable that it is single (100) orientation, and even when it is any, it is more desirable that it is an epitaxial film. If such a good crystalline zirconium-oxide system thin film can be formed, the disturbance of the physical quantity by the grain boundary etc. will be lost, and a good insulating ground thin film, a conductive ground thin film, and a ferroelectric thin film will be obtained on a zirconium-oxide system thin film.
[0048] When the laminating of a middle thin film (Zr1-x Rx O2-delta) and the insulating ground thin film (BaTiO3) is carried out to Si (100) substrate front face one by one, these orientation relationships BaTiO3/(001)/Zr1-x Rx O2-delta(001)// Si (100), and BaTiO3 It is desirable that they are [100]//Zr1-x Rx O2-delta[100]// Si [010]. Although this is the case where each of middle thin films and insulating ground thin films is tetragonal phases, even when these thin films are cubics, it is the same at the point that it is desirable that shafts are parallel in a field.
[0049] By the analogy from the conventional examples, such as YBCO, it is BaTiO3 of orientation (001). When it is going to obtain an epitaxial film, the orientation relationship BaTiO3/(001)/Zr1-x Rx O2-delta(001)// Si (100), And BaTiO3 It is set to [110]//Zr1-x Rx O2-delta[100]// Si [010], and is BaTiO3. It is presumed that 45 degrees rotates within the c-th page to the grid of Zr1-x Rx O2-delta, and a unit lattice can take adjustment of a grid, and grows epitaxially. However, according to the experiment of this invention persons, composition is difficult and such an orientation relationship is BaTiO3/ (001)/Zr1-x Rx O2-delta(001)// Si (100), and BaTiO3. It found out that it could constitute from relation between [100]//Zr1-x Rx O2-delta[100]// Si [010].
[0050] Namely, the lattice constant of an a-axis is 0.52 by the Zr1-x Rx O2-delta film, and is BaTiO3. BaTiO3 which rotates and carries out grid adjustment in 45-degree side although it is 0.40 by the film In the relation between [110]//Zr1-x Rx O2-delta[100]// Si [010], misfit becomes 8.4%. However, grid adjustment relation BaTiO3 by this invention In [100]//Zr1-x Rx O2-delta[100]// Si [010] BaTiO3 The a-th page of a crystal and the a-th page of a Zr1-x Rx O2-delta crystal are adjusted as they are, without rotating, and BaTiO3 4 grid (0.4x4=1.60[nm]) adjusts it to Zr1-x Rx O2-delta3 grid (0.52x3=1.56[nm]) in this case. At this time, misfit is well matched with 2.6%. Therefore, at this invention, it is BaTiO3. By using the relation between [100]//Zr1-x Rx O2-delta[100]// Si [010], it is epitaxial BaTiO3 of orientation (001). A film can be obtained.
[0051] ZrO2 It applies to a room temperature from an elevated temperature, and cubic -> tetragonal -> monoclinic system and phase transition are produced. It is the stabilized zirconia which added rare earth elements in order to stabilize a cubic. It depends for the crystallinity of a Zr1-x Rx O2-delta film on the range of x. Jpn.J.Appl.Phys.27 x becomes a tetragonal phase or a monoclinic system crystal in the composition region which is less than 0.2 as reported to (8) L1404-L1405 (1988). Until now, in two or more cubic fields, the epitaxial film of single orientation is obtained for x. However, although x is a cubic in the field exceeding 0.75, single orientation is not acquired but the crystal of orientation (111) mixes it, for example (100). On the other hand, in the field used as a tetragonal phase or monoclinic system, it is J.Appl.Phys.58. (6) Orientation sides other than what it is going to obtain mix, and the epitaxial film of single orientation is not obtained as stated also to 2407-2409 (1985).
[0052] Therefore, as for x, from the point of crystal orientation, it is desirable in Zr1-x Rx O2-delta that it is 0.2-0.75. The more desirable ranges of x are 0.2-0.50. If a zirconium-oxide system thin film is an epitaxial film, it will be easy to grow epitaxially the insulating ground thin film and ferroelectric thin

film which are formed on it.
[0053] In order for the rare earth elements which a stabilized zirconia contains to make the lattice constant of the thin film prepared on the lattice constant of Si substrate, and a zirconium-oxide system thin film, and the lattice constant of a zirconium-oxide system thin film match preferably, the kind and addition are chosen. For example, as for with an above-mentioned lattice constant of 0.52nm Zr1-x Rx O2-delta, R is Y and x is the thing of 0.3. Although a lattice constant is changeable if x is changed with the kind of R fixed, the field of matching in change of only x which can be adjusted is narrow. When it changes to Y and Pr is used here, it is possible to enlarge a lattice constant and it is BaTiO3 of an insulating ground thin film. Matching with a crystal can be optimized.
[0054] In addition, the zirconium oxide which does not include an oxygen defect is a chemical formula ZrO2. Although expressed, it becomes the range in which the amount of oxygen changed and usually described above delta in Zr1-x Rx O2-delta with the kind, amount, and valence of the rare earth elements which added the zirconium oxide which added rare earth elements.
[0055] In Zr1-x Rx O2-delta, as mentioned above, crystallinity did not become fitness, and good front-face nature was not obtained in the field whose x is less than 0.2, and especially the composition region of a high grade where the ratio of Zr in the composition element except oxygen exceeds 93-mol%, either. However, as a result of this invention persons' repeating examination, by applying the manufacture method mentioned later showed the above-mentioned single orientation and that epitaxial growth became still more possible and a value also with good front-face nature was acquired. ZrO2 of a high grade There is a merit which is described below in a film.
[0056] It is ZrO2, so that the ratio of Zr in the composition element except oxygen is high. It is desirable, when insulation resistance also becomes high and a leakage current also needs an insulating property from a bird clapper small so that purity is high. Moreover, it sets in metal-insulator-semiconductor structure (MIS structure), and is ZrO2. Since the hysteresis of the C-V property of seeing when YSZ (Y stabilized zirconia) is used as an insulator is lost when it uses as an insulator, an interface property is excellent as an MIS element. As this reason, the stress generated by the difference in a coefficient of thermal expansion between Si substrate and a zirconium-oxide system thin film is ZrO2. Being eased by phase transition and ZrO2 It is possible that there are few oxygen defects. Since stress was not eased since there was no phase transition, and YSZ has added rare earth elements, it has many oxygen defects. Moreover, it also sets in MFMIS structure or MFIS structure, and is ZrO2 as an insulator. Since the C-V hysteresis of information-separator portion is lost when it uses, the C-V hysteresis by polarization reversal of a ferroelectric is acquired effectively, and is desirable.
[0057] therefore, the ratio of Zr in the composition element excluding the oxygen in a zirconium-oxide system thin film when good crystallinity and front-face nature are obtained -- desirable -- 93mol% ** -- more -- desirable -- more than 95mol% -- further -- desirable -- more than 98mol% -- it is more than 99.5mol% most preferably Oxygen and the composition element except Zr are usually rare earth elements, P, etc. In addition, now, the upper limit of the ratio of Zr is about 99.99mol%. Moreover, with the present high grade-ized technology, it is ZrO2. HfO2 Since it is difficult, separation is ZrO2. Purity has usually pointed out the purity in Zr+Hf. Therefore, ZrO2 in this specification Purity is HfO2 although it is the value computed by having considered that Hf and Zr were these elements. It sets to the zirconium-oxide system thin film in this invention, and is ZrO2. Completely, in order to function similarly, it is satisfactory.
[0058] in addition, when forming a middle thin film, the oxygen in a middle thin film is spread near the substrate front face of Si single crystal substrate, and near a substrate front face oxidizes shallowly (for example, about 5nm or less) -- having -- SiO2 etc. -- an oxidizing zone may be formed Moreover, depending on the method of membrane formation, Si oxide layer may remain on Si substrate front face at the time of middle thin film formation.
[0059] As the rare earth oxide system thin film above was carried out, when the stabilized zirconia described above as a middle thin film is used, a hysteresis is seen by the C-V property and it sets at this point, and it is ZrO2. It is inferior to a high grade film. In this case, the hysteresis of a C-V property can be abolished by carrying out the laminating of the rare earth oxide system thin film on a zirconium-

oxide system thin film. Moreover, matching of the grid adjustment between ferroelectric thin films becomes better by carrying out the laminating of the rare earth oxide system thin film.
[0060] In addition, a rare earth oxide system thin film is formed on a zirconium-oxide system thin film because the film of single (001) orientation or single (100) orientation cannot be formed but it becomes the film of cubic orientation (111) only by the rare earth oxide system thin film.
[0061] As for a rare earth oxide system thin film, it is desirable to consist of substantially rare earth oxides of Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu which contain at least one sort of Ce, Pr, Nd, Gd, Tb, Dy, Ho, and Er especially at least one sort. In addition, the ratio is arbitrary when using two or more sorts of rare earth elements.
[0062] When the laminating of the rare earth oxide system thin film is carried out, an element distribution may be a uniform film and a zirconium-oxide system thin film may be an inclination structure film from which composition changes in the direction of thickness. When considering as an inclination structure film, while applying to a rare earth oxide system thin film side from a substrate side and increasing gradually or gradually the rare-earth-elements content in a zirconium-oxide system thin film, Zr content is decreased gradually or gradually. By considering as such an inclination structure film, it becomes easy for the misfit of the grid between a zirconium-oxide system thin film and a rare earth oxide system thin film to become small, or to stop existing, and to make a rare earth oxide system thin film into the epitaxial film of high crystallinity.
[0063] In addition, as for the rare earth elements added to a rare earth oxide system thin film, it is desirable to use the same thing as the rare earth elements added to a zirconium-oxide system thin film.
[0064] You may introduce an additive into a zirconium-oxide system thin film and a rare earth oxide system thin film for a property improvement. For example, if alkaline-earth elements, such as calcium and Mg, are doped to these thin films, a membranous pinhole can decrease and leak can be suppressed. Moreover, aluminum and Si are effective in raising membranous resistivity. Furthermore, transition-metals elements, such as Mn, Fe, Co, and nickel, can form the level (trap level) by the impurity into a film, and conductive control is attained by using this level.
[0065] In order that a <crystallinity [of each thin film], front-face nature, and thickness> ground thin film and a middle thin film may raise the crystallinity of the thin film formed on it, its crystallinity is good and it is desirable that a front face is flat.
[0066] The half-value width of the rocking curve of the reflective peak in XRD (X diffraction) and the pattern of the image by RHEED can investigate the crystallinity of a thin film. Moreover, front-face nature can be investigated by the streak nature of a RHEED image, and the surface roughness (ten-point average of roughness height) measured by AFM.
[0067] As for the crystallinity of an insulating ground thin film, a conductive ground thin film, and a middle thin film, it is desirable that it is that from which the half-value width of the rocking curve of reflection of the field by the X diffraction (002) becomes 1.50 degrees or less. Moreover, about an insulating ground thin film and a middle thin film, when surface roughness Rz (the ten-point average of roughness height, a criteria length of 500nm) is measured by AFM, it is desirable that it is 2nm or less, and it is more desirable that it is 0.60nm or less. Moreover, as for the above Rz of a conductive ground thin film, it is desirable that it is 10nm or less. In addition, the front face of each thin film is desirable, and, as for such surface roughness, it is more preferably desirable to have realized in 95% or more of field still more preferably 90% or more 80% or more. The above-mentioned surface roughness is 2 an area of 10cm. When each thin film is formed over the whole substrate surface, it is the value which measures ten or more arbitrary places distributed over the average.
[0068] Although there are not half-value width of a rocking curve and especially a lower limit of Rz, and it is so desirable that it is small, now, the lower limit of the ten-point average of roughness height Rz with about 0.4 degrees and a criteria length of 500nm of the lower limit of the half-value width of a rocking curve is about 0.10nm.
[0069] A RHEED image is a streak, and moreover, when sharp, the crystallinity of each thin film and surface flat nature will be excellent.
[0070] The thickness of an insulating ground thin film changes with uses, and generally, although it is

50-150nm more preferably, it is preferably desirable that it is thin to the grade by which crystallinity and front-face nature are not spoiled 5-500nm. Moreover, as for the thickness in the case of using an insulating ground thin film as an insulating layer, it is desirable that it is about 50-500nm.
[0071] The thickness of a conductive ground thin film also changes with uses, and generally, although it is about 50-150nm more preferably, it is preferably desirable that it is thin to the grade by which crystallinity and front-face nature are not spoiled 5-500nm. When operating a conductive ground thin film as an electrode layer, it is desirable to set thickness to about 50-500nm.
[0072] The thickness of a middle thin film also changes with uses, and generally, although it is 10-50nm more preferably, it is preferably desirable that it is thin to the grade which does not spoil crystallinity and front-face nature 5-500nm. Moreover, as for the thickness in the case of using a middle thin film as an insulating layer, it is desirable that it is about 50-500nm. In addition, when considering as the two-layer composition which described the middle thin film above, as for the thickness of each thin film, it is desirable that it is 0.5nm or more, and, as for the thickness of the whole middle thin film, considering as the above-mentioned range is desirable.
[0073] When a ferroelectric thin film front face is measured by AFM like the above, 10nm or less of Rz (es) with a criteria length of 500nm is 5nm or less more preferably. There is, and especially the lower limit of Rz is so desirable that it is small. [no] Since the capacity of memory is proportional to the number of bits when a ferroelectric thin film constitutes memory, in order to consider as a bulk memory, it is necessary to increase the number of bits per unit area. Since record becomes possible even if the front-face nature of a ferroelectric thin film carries out bit area to it being good small, the surface disposition top is effective at the point which increases the number of bits per unit area. Now, the lower limit of Above Rz is about 1nm.
[0074] The membrane structure object of a <electron device> this invention is processed according to a semiconductor process, is constituted as the gate of a capacitor and FET, and let them be electron devices, such as non-volatile memory and an infrared sensor. Moreover, it is applicable to an optical modulator, an optical switch, OEIC, etc.
[0075] The membrane structure object of a <record-medium> this invention is applicable also to the record medium which records information with probes, such as AFM and STM (scanning tunneling microscope). The method of recording on a ferroelectric with probes, such as AFM, is indicated by JP,63-193349,A. On the occasion of record, first, voltage is impressed to a ferroelectric thin film with probes, such as AFM, and only the field by which the probe was carried out reverses polarization. The field by which polarization reversal was carried out serves as a record bit, and will support information. The piezoelectricity effect of a ferroelectric, a pyroelectric effect, the electro-optical effect, the current detection at the time of polarization reversal, etc. are used for read-out of information. Specifically, RF bias voltage is impressed to a record medium and a probe, and it scans with a probe. At this time, a record intermediation body surface deforms by the piezoelectricity effect of a ferroelectric thin film. Since the direction of polarization is reverse, piezoelectricity effects differ in a record bit field and a non-record section. For this reason, in a record-medium front face, the deformation according to existence of a record bit appears, and a record bit can be discriminated by detecting this deformation with a probe. What is necessary is to impress the pulse voltage of reversed polarity with the time of record, and just to reverse polarization, when eliminating a record bit.
[0076] In addition, the membrane structure object of this invention with which such a record reproduction method is applied is the thing of FMIS structure or FIS structure. Since it is necessary to impress electric field to a ferroelectric thin film at the time of record reproduction, in using the thing of FIS structure, generally it operates this as a lower electrode using a substrate with high conductivity.
[0077] Moreover, if the ferroelectric thin film is formed on Si substrate, capture of the charge by polarization reversal and a discharge phenomenon can be used, and a depletion layer can be formed by the charge captured by Si substrate which is a semiconductor. If such a depletion layer is formed, since capacity will change, it can consider as a record bit. Read-out in this case impresses RF bias voltage to a record medium and a probe like the above, and is performed by scanning with a probe. Since the field where charge capture is made differs in the capacity between a probe and a record medium from the

field which is not made, a record bit is discriminable by detecting this capacity change. Elimination of a record bit can be performed like the above.

[0078] In addition, by this record reproduction method, electric field are impressed through the semiconductor section, using the membrane structure object of FIS structure as a record medium.

[0079] AFM and STM have the resolution of atomic level. Moreover, since polarization reversal speed is as high-speed as 100 or less ns and it is possible to form a record bit with the size below 10nmphi, a ferroelectric is 2 100 megabits/cm. Realization of the above high-density memory is expected. In this invention, since the very good ferroelectric thin film of front-face nature is obtained, such high-density memory is realizable.

[0080] The <manufacture method of a ferroelectric thin film>, next the manufacture method of the ferroelectric thin film of this invention are explained in detail.

[0081] In addition, in enforcing the manufacture method of this invention, it is desirable to use vacuum evaporationo equipment 1 as shown in drawing 1 . Here, it is $PbTiO_3$ as a lead system ferroelectric thin film. Although the PGT thin film which is the composition which added Gd is mentioned as an example and explained, the thin film which consists of other lead system ferroelectric material can be manufactured similarly.

[0082] Vacuum evaporationo equipment 1 has vacuum tub 1a in which vacuum pump P was prepared, and the electrode holder 3 which holds a substrate 2 in the lower part is arranged in this vacuum tub 1a. It connects with the motor 5 through the axis of rotation 4, and can rotate by this motor 5, and this electrode holder 3 can rotate a substrate 2 now in the field. The above-mentioned electrode holder 3 builds in the heater 6 which heats a substrate 2.

[0083] Vacuum evaporationo equipment 1 is equipped with the oxidizing gas feeder 7, and, as for the oxidizing gas feed hopper 8 of this oxidizing gas feeder 7, the above-mentioned electrode holder 3 is arranged immediately caudad. As for a oxidizing gas, the partial pressure is made high by about two substrate by this. In a lower part, they are the PbO evaporator 9 and TiOx to the pan of a electrode holder 3. The evaporator 10 and the rare-earth-elements evaporator 11 are arranged. The energy feeders (an electron ray generator, resistance heating equipment, etc.) for supplying the energy for evaporation other than each evaporation source are arranged at each [these] evaporator.

[0084] The reason using an oxide (PbO) as a lead evaporation source is that deposit efficiency will increase if PbO is used although it re-evaporates if Pb is used for an evaporation source and is hard to adhere to a substrate front face on a hot substrate, since the vapor pressure of Pb is high, and is TiOx. The reason for using is also that deposit efficiency is high similarly. TiOx When Ti is used instead, in order that Ti may tend to oxidize rather than PbO, since oxygen is taken by Ti, PbO serves as Pb and this re-evaporates it, it is not desirable.

[0085] in addition, TiOx x which can be set -- desirable -- $1<=x<1.9$ -- more -- desirable -- $1<=x<1.8$ -- further -- desirable -- $1.5<=x<=1.75$ -- it is $1.66<=x<=1.75$ especially preferably Such TiOx If heat energy is applied, it will fuse within a vacuum tub and the stable vapor rate will be obtained. On the other hand, TiO_2 It is TiOx, emitting oxygen within a vacuum tub, if heat energy is applied. Since the vapor rate which the pressure fluctuation in a vacuum tub became large, and was stabilized in order to change is not obtained, composition control is impossible.

[0086] First, a substrate is set to the above-mentioned electrode holder. Although various kinds of things mentioned above can be used for substrate material, among these, Si single crystal substrate is desirable. It is desirable to use especially the field (100) of Si single crystal so that it may become a substrate front face. Moreover, it is also desirable to use as a substrate the single crystal board in which said middle thin film, the insulating ground thin film, the conductive ground thin film, etc. were formed.

[0087] By the manufacture method of this invention, it is a large area substrate, 10cm2 [for example,], about a homogeneous ferroelectric thin film. It can form on a substrate with the above area. Thereby, let the electron device and record medium which have a ferroelectric thin film be a very cheap thing compared with the former. In addition, especially the upper limit of the area of a substrate is 2 400cm in the present condition, although there is nothing. It is a grade. Although the present semiconductor process has 2-8 inches Si wafer and a thing especially in use using the 6 inch type wafer, this invention

can respond to this. Moreover, it is also possible not the whole wafer surface but to choose with a mask etc. partially and to form a ferroelectric thin film.
[0088] Next, a substrate is heated in a vacuum and they are PbO and TiOx. And the ferroelectric thin film is formed by supplying Gd and a oxidizing gas to a substrate front face.
[0089] As for especially heating temperature, it is desirable to consider as 550-650 degrees C 500-700 degrees C. A crystalline high ferroelectric thin film is it hard to be obtained to be less than 500 degrees C. If it exceeds 700 degrees C, Si of a lead steam and a substrate etc. will react and a crystalline lead system ferroelectric film will be hard to be obtained. Moreover, when forming a ferroelectric thin film on conductive ground thin films, such as Pt, a reaction with Pt will arise.
[0090] As the above-mentioned oxidizing gas, although oxygen, ozone, atom-like oxygen, NO2, radical oxygen, etc. can be used, it is desirable to consider as the oxygen which radical-ized most most [parts or].
[0091] Here, the case where the radical oxygen by the source of efficient consumer response oxygen is used is explained.
[0092] Most supplies the radical-ized oxygen gas continuously in a vacuum deposition tub from the source of efficient consumer response oxygen, exhausting the inside of a vacuum tub continuously with a vacuum pump. As for oxygen tension [near the substrate], it is desirable that it is about 10-3 to 10 to 1 Torr. The upper limit of oxygen tension was set to 10-1Torr for keeping the vapor rate constant, without degrading the metal in the evaporation source in a vacuum tub. It faces introducing oxygen gas into a vacuum deposition tub, and gas is injected from the near on the surface of a substrate, it can be good to build the atmosphere of high oxygen tension only near the substrate, and, thereby, the reaction on a substrate can be promoted more in the few amount of gas introduction. Since the inside of a vacuum tub is continuously exhausted at this time, almost all the portions of a vacuum tub have a low pressure of 10-4 - 10-6Torr. The amount of supply of oxygen gas is a part for 5-25 cc/preferably by 2-50 cc/. Since the optimal amount of supply of oxygen gas is decided by the capacity of a vacuum tub, and the factor of a pumping speed and others, it calculates the suitable amount of supply beforehand.
[0093] With an electron beam etc., each evaporation source is heated, is evaporated, and is supplied to a substrate. Membrane formation speed is 0.100 - 0.500 nm/s more preferably 0.05 to 1.00 nm/s. If membrane formation speed is too slow, it will become difficult to keep membrane formation speed constant, and a film will tend to become heterogeneous. On the other hand, if membrane formation speed is too quick, the crystallinity of the thin film formed is bad and irregularity will arise on a front face.
[0094] TiOx And what is necessary is just to supply it on a substrate with the vapor rate of the ratio corresponding to the composition ratio made into the purpose, since Gd is incorporated by the PGT crystal as which it supplied and as which the whole quantity grows on a substrate mostly. However, since vapor pressure is high, PbO tends to cause a composition gap, and control is difficult for it. With the ferroelectric material of a lead system, there is no composition gap and the thin film more near a single crystal is not obtained until now. In this invention, this property of PbO is used conversely and the amount-of-supply ratio to the substrate from a PbO evaporation source is made superfluous to the ratio in the PGT film crystal formed. atomic-ratio Pb/Ti=E (Pb/Ti) of Pb and Ti to which the degree of overage is supplied from an evaporation source Atomic-ratio Pb/Ti=F (Pb/Ti) of Pb and Ti in composition of the formed ferroelectric thin film, a relation -- E (Pb/Ti)/F (Pb/Ti) =1.5-3.5 -- they are E (Pb/Ti)/F (Pb/Ti) =1.7-2.5 and the thing more preferably set to E (Pb/Ti)/F (Pb/Ti) =1.9-2.3 preferably PbO which is not included in superfluous PbO or a superfluous perovskite structure will be re-evaporated on a substrate front face, and only the PGT film of a perovskite structure will grow on a substrate. E (Pb/Ti)/F (Pb/Ti) If too small, it becomes difficult to fully supply Pb into a film, and the ratio of (Pb+Rn)/Ti in a film will become low too much, and will not serve as a crystalline high perovskite structure. On the other hand, it is E (Pb/Ti)/F (Pb/Ti). If too large, the ratio of (Pb+Rn)/Ti in a film will become large too much, other Pb rich phases will appear besides a perovskite phase, and perovskite single phase structure will no longer be acquired.
[0095] As explained above, they are PbO and TiOx. By using as an evaporation source, raising deposit

efficiency, and oxidizing powerfully by radical oxygen, and setting substrate temperature as the predetermined range, the excess and deficiency of Pb twist and the PGT crystal of a stoichiometry grows up to be a self-adjustment target on a substrate mostly. This method is an epoch-making method of manufacturing the lead system perovskite crystal thin film of a stoichiometry, and a crystalline, very high ferroelectric thin film is obtained.

[0096] Membrane formation area is 2 10cm. When forming membranes on the front face of a substrate with a diameter of 2 inches when it is beyond a grade for example, oxidation reaction can be promoted throughout a membrane formation field by rotating a substrate, as shown in drawing 1 , and supplying a oxidizing gas uniformly throughout a substrate front face. Thereby, moreover, formation of a homogeneous film is attained by the large area. At this time, the rotational frequency of a substrate is 10rpm. It is desirable that it is above. If a rotational frequency is low, it will be easy to produce the distribution of thickness in a substrate side. Especially the upper limit of the rotational frequency of a substrate is usually mechanism top 120rpm of vacuum devices, although there is nothing. It becomes a grade.

[0097] It is desirable after ferroelectric thin film formation to give annealing if needed. Preferably, 500-850 degrees C, annealing is 650-800 degrees C more preferably, and is performed for 5 - 15 minutes for [for / 1 second / -] 30 minutes. Although orientation (100) may appear (100) or the rate of orientation may increase when a ferroelectric thin film is annealed, generally the property as a ferroelectric improves by annealing. In addition, although it prepares an electrode layer on a ferroelectric thin film in considering as MFMIS structure or MFIS structure, in such a case, annealing may be performed before formation of an electrode layer and may be performed after formation. Since annealing is performed after crystallization, there are no worries about the composition gap by annealing.

[0098] As mentioned above, although the detail of the manufacture method of a ferroelectric thin film was explained, since this manufacture method can be enforced especially in comparison with the conventional vacuum deposition method, the sputtering method, the laser abrasion method, etc. under the operating condition which does not have the room of an intervention of an impurity so that clearly and which is moreover easy to control, it is suitable to obtain the specified substance with good repeatability and high integrity by the large area.

[0099] Even if it furthermore uses MBE equipment in this method, the target thin film can completely be obtained similarly.

[0100] Although how to manufacture the thin film of the rare-earth-elements addition lead-titanate system which is the ferroelectric thin film which the membrane structure object of this invention has was described above, this method can be applied to PT system material which does not add rare earth elements, PZT system material, etc., and the same effect is acquired also by these cases. Moreover, it is applicable also to Bi system oxide thin film. Also in Bi system oxide thin film, since the vapor pressure of Bi was high, although composition control was inadequate in the vacuum until now, it sets by this invention method, and it is Bi 2O3 about a PbO evaporation source. It is checking that it can manufacture similarly by changing to an evaporation source. It is incorporated by the self-adjustment target at a crystal that Bi is not in Bi system, and the ferroelectric thin film crystal of a stoichiometry is obtained.

[0101] The <manufacture method of a membrane structure object>, next the manufacture method of the membrane structure object of this invention are explained.

[0102] When using a substrate surface treatment Si single crystal substrate, it is desirable to perform surface treatment to a substrate before formation of a middle thin film. Below, the need for surface treatment is explained.

[0103] Generally the surface structure in the number atomic layer on the front face of a crystal differs from the atomic-arrangement structure of the imagination front face considered when the crystal structure of bulk (big 3-dimensional-like crystal) is cut. This is because the situation around the atom which appeared in the front face when the crystal of one side stopped there not being tends to change and it is going to be in the lower stable state of energy corresponding to this. The case where it stops at relief of an atomic position, and recombination of an atom mainly arise, and the structural change may

form rearrangement structure. The former exists on almost all the crystal front face. Generally the latter forms a superstructure in a front face. This is called mxn structure, when setting the size of the unit vector of the surface structure of bulk to a and b and the superstructure of the size of ma and nb arises.
[0104] In order to grow an oxide thin film epitaxially on Si substrate, the structure of Si substrate front face is stable, and the role which Si substrate front face reports that the crystal structure information is to the oxide thin film to grow up must be played. Since the atomic-arrangement structure considered when the bulk crystal structure is cut is 1x1 structure, the surface structure of the substrate for growing an oxide thin film epitaxially needs to be 1x1 stable structure.
[0105] However, since the front face of Si (100) which it defecated serves as 1x2 or 2x1 structure so that it may mention later, and the front face of Si (111) becomes complicated super-structure with the big unit mesh of 7x7 or 2x8 structure, it is not desirable.
[0106] Moreover, these Si front faces that it defecated are rich in reactivity, the residual gas especially hydrocarbon, and reaction in a vacuum are caused, by forming SiC in a front face, a substrate front face is polluted especially with the temperature (700 degrees C or more) which carries out epitaxial formation of the oxide thin film, and a surface crystal is confused at it. Therefore, on the occasion of formation of an oxide thin film, it is necessary to protect Si front face which was rich in reactivity.
[0107] Since it is such, it is desirable to perform surface treatment to Si single crystal substrate by the following methods.
[0108] By this method, it sets to the electrode holder which shows Si single crystal substrate which defecated the front face first to drawing 1 , and arranges in a vacuum tub, and it heats, introducing a oxidizing gas, and Si oxide layer is formed in a substrate front face. You may use air, although the thing same as a oxidizing gas as the case of the above-mentioned ferroelectric thin film can be used. Si oxide layer is for protecting a substrate front face from a rearrangement, contamination, etc. As for the thickness of Si oxide layer, it is desirable to be referred to as about 0.2-10nm. It is because protection of Si front face becomes imperfect for thickness to be less than 0.2nm. The reason for having set the upper limit to 10nm is mentioned later.
[0109] Grade maintenance is carried out for 0 - 10 minutes, and the above-mentioned heating is performed to the temperature of 300-700 degrees C. At this time, a programming rate is carried out in about 30-70 degrees C/minute. Conversely, temperature is too high, or if a programming rate is too quick, formation of Si oxide layer will become inadequate, and temperature will be too low, or if the holding time is too long, Si oxide layer will become thick too much.
[0110] When using oxygen as a oxidizing gas, as for introduction of a oxidizing gas, it is desirable that make the inside of a vacuum tub into the vacuum of about 1x10-7 to 1x10 to 4 Torrs at the beginning, and the oxygen tension in the atmosphere near the substrate carries out by [as being set to 1x10-4 - 1x10-1Torr] at least by introduction of a oxidizing gas.
[0111] It heats in a vacuum after the above-mentioned process. Since Si crystal on the front face of a substrate is protected by Si oxide layer, it reacts with the hydrocarbon which is residual gas, and contamination of SiC being formed does not generate it. As for especially heating temperature, it is desirable to consider as 700-1100 degrees C 600-1200 degrees C. 1x1 structure is not acquired on Si single crystal substrate front face as it is less than 600 degrees C. If it exceeds 1200 degrees C, protection of Si crystal by Si oxide layer becomes less enough, and the crystallinity of Si single crystal substrate will be confused.
[0112] Subsequently, Zr and a oxidizing gas, Zr and rare earth elements (Sc and Y are included), and a oxidizing gas are supplied to a substrate front face. In this process, metals, such as Zr, will return and remove Si oxide layer formed at the last process. The surface structure of 1x1 is formed in Si crystal front face exposed simultaneously of Zr and oxygen or Zr, rare earth elements, and oxygen.
[0113] The pattern of the image by RHEED can investigate a surface structure. For example, in the case of the surface structure of 1x1 which is desirable structure, the direction of electron ray incidence serves as a perfect streak pattern of the 1 time period C1 as shown in drawing 17 (a) by [110], and serves as the pattern completely same as for [1-10] in the direction of incidence. On the other hand, Si single crystal clean surface serves as a surface structure in which it is 1x2 or 2x1 in the case of a field (100), or 1x2

and 2x1 are intermingled. In such a case, the pattern of RHEED is the direction of incidence of an electron ray [110], either of [1-10], or both, and turns into a pattern with the 1 time period C1 as shown in drawing 17 (b), and the double-precision period C2. In the surface structure of 1x1, it sees by the pattern of Above RHEED, and the directions of incidence are both [110] and [1-10], and the double-precision period C2 is not seen.
[0114] In addition, Si (100) clean surface may also show 1x1 structure, and our experiment was also observed several times. However, the conditions which show 1x1 are indefinite, and it is impossible in the present condition to obtain 1x1 with stably sufficient repeatability in respect of Si pure. 1x2, 2x1, and 1x1 -- even if it is the case of which structure, Si pure side is easy to be polluted with an elevated temperature among a vacuum, it reacts with the hydrocarbon contained especially in residual gas, SiC is formed, and the crystal on the front face of a substrate tends to be confused
[0115] As for Zr or Zr, and rare earth elements, it is desirable that the thickness when carrying out the vacuum evaporationo of these in an oxidizing atmosphere, and forming an oxide film supplies 0.3-10nm so that it may be especially set to about 3-7nm. The display of such the amount of supply is hereafter called amount of supply in oxide conversion. if the effect of reduction of Si oxide of the amount of supply in oxide conversion in less than 0.3nm cannot fully demonstrate but exceeds 10nm -- a front face -- the irregularity of atomic level -- generating -- being easy -- the array which is a surface crystal may be no longer 1x1 structure by irregularity The reason for having set the desirable value of the upper limit of the thickness of the above-mentioned Si oxide layer to 10nm is that possibility that it becomes impossible to fully return Si oxide layer will come out even if it supplies a metal as mentioned above if it exceeds 10nm.
[0116] When using oxygen as a oxidizing gas, it is desirable to supply about 2-50cc /a minute. Since the optimal amount of supply of a oxidizing gas is decided by the capacity of a vacuum tub, and the factor of a pumping speed and others, it calculates the optimal amount of supply beforehand.
[0117] As for a zirconium-oxide system thin film, it is desirable among the formation middle thin films of a middle thin film to form by the method which these people already proposed in Japanese Patent Application No. No. 93024 [seven to].
[0118] In formation of a thin film, a substrate is heated first. As for the heating temperature at the time of membrane formation, it is desirable that it is 400 degrees C or more because of crystallization of a zirconium oxide, and if it is 750 degrees C or more, in order to obtain the film excellent in crystallinity and to obtain the surface flat nature of molecule level especially, it is desirable that it is 850 degrees C or more. In addition, the upper limit of the heating temperature of a single crystal substrate is about 1300 degrees C.
[0119] Subsequently, while heating Zr, evaporating it with an electron beam etc. and supplying a substrate front face, rare earth elements are supplied to a substrate front face a oxidizing gas and if needed, and a zirconium-oxide system thin film is formed. Membrane formation speed is more preferably made into 0.100 - 0.500 nm/s 0.05 to 1.00 nm/s. If membrane formation speed is too slow, it will become difficult to keep membrane formation speed constant, on the other hand, if membrane formation speed is too quick, the crystallinity of the thin film formed will become bad and irregularity will arise on a front face.
[0120] In addition, about various conditions, such as oxygen tension the kind of oxidizing gas, its amount of supply, and near the substrate, and rotation of a substrate, it is the same as that of the case of the above-mentioned ferroelectric thin film formation.
[0121] What is necessary is to use only rare earth elements as an evaporation source, when carrying out the laminating of the rare earth oxide system thin film on a zirconium-oxide system thin film. The introductory conditions of the oxidizing gas at this time, the temperature conditions of a substrate, etc. are good like the case of a zirconium-oxide system thin film then. When using the same rare earth elements in both thin films, when a zirconium-oxide system thin film is formed in predetermined thickness, supply of Zr can be stopped, and a rare earth oxide system thin film can be continuously formed by supplying only a rare earth metal succeedingly. Moreover, what is necessary is to reduce the amount of supply of Zr gradually and just to shift to formation of a rare earth oxide system thin film as

zero finally, in making a zirconium-oxide system thin film into inclination structure.
[0122] It is BaTiO3 as an insulating ground thin film on an insulating ground thin film middle thin film. The case where a film is formed is explained.
[0123] Ba and Ti are supplied to a substrate front face after middle thin film membrane formation, continuing heating and introduction of a oxidizing gas. As for the amount of supply, it is desirable to make it set to Ba:Ti=1:1. The temperature of the vacuum evaporationo substrate at the time of membrane formation and the Ba/Ti amount-of-supply ratio in early stages of membrane formation are BaTiO3. A membranous stacking tendency is affected. BaTiO3 The orientation relationship of a film, a middle thin film (Zr1-x Rx O2-delta), and Si (100) substrate The desirable relation mentioned above, i.e., BaTiO3/(001)/Zr1-x Rx O2-delta(001)//Si, (100) And BaTiO3 It is BaTiO3 in order to make it set to [100]//Zr1-x Rx O2-delta[100]// Si [010]. The heating temperature at the time of membrane formation has preferably desirable 900-1200 degrees C 800-1300 degrees C. Moreover, it is desirable 1-0, and for the Ba/Ti amount-of-supply ratio in early stages of growth to set to 1-0.8 preferably. That is, it is desirable to **** to overTi in early stages of growth. In addition, it is shown that you may be it supply of only Ti that a Ba/Ti amount-of-supply ratio is 0 in early stages of growth. If heating temperature is too high, counter diffusion will arise in a thin film layered product, and crystallinity will fall. BaTiO3 which will be formed on the other hand if heating temperature is too low or the Ba/Ti ratio in early stages of growth is not suitable A film becomes the orientation instead of orientation (110) made into the purpose (001), or (001) it is orientation BaTiO3. An orientation (110) crystal will be intermingled on a film. BaTiO3 which supplied Ba reacts with the zirconium-oxide system thin film of a ground in early stages of growth, and has the target orientation It is hard to be obtained. Suppose that Ti is superfluous in early stages of growth for avoiding the reaction of Ba and a zirconium oxide. In addition, thickness is within the limits which is about 1nm or less the early stages here of growth.
[0124] About various conditions, such as oxygen tension the membrane formation speed at the time of insulating ground thin film formation, the kind of oxidizing gas, its amount of supply, and near the substrate, and rotation of a substrate, it is the same as that of the case of the above-mentioned zirconium-oxide system thin film formation.
[0125] As well as the case of the above-mentioned ferroelectric thin film since it can enforce the above-mentioned formation method of a middle thin film or an insulating ground thin film especially in comparison with the conventional vacuum deposition method, the sputtering method, the laser abrasion method, etc. under the operating condition which does not have the room of an intervention of an impurity so that clearly and which is moreover easy to control, it is suitable to obtain the specified substance with good repeatability and high integrity by the large area. Even if it uses MBE equipment in the above-mentioned method, the target thin film can completely be obtained similarly.
[0126] When it constitutes from a conductive ground thin film metal, forming by vacuum evaporationo is desirable. As for the substrate temperature at the time of vacuum evaporationo, it is desirable to consider as 500-750 degrees C. If substrate temperature is too low, a crystalline high film will not be obtained, but if substrate temperature is too high, the irregularity of a membranous front face will become large. In addition, crystallinity can be further raised by introducing Rf plasma, passing the oxygen of a minute amount in a vacuum tub at the time of vacuum evaporationo. There is an effect which specifically prevents orientation (111) mixing into orientation (001) in Pt thin film.
[0127] When it constitutes from the oxide or the conductive perovskite oxide containing In, it is desirable to use the above-mentioned formation method of a ferroelectric thin film or an insulating ground thin film, in addition it can also use reactant plural vacuum depositions and a spatter.
[0128] About the ferroelectric thin film in the ferroelectric thin film film structure, it is desirable to form by the above-mentioned manufacture method of a ferroelectric thin film.
[0129]
[Example] Hereafter, the concrete example of this invention is shown and this invention is further explained to a detail.
[0130] Pt (001) orientation film was formed in the front face of cutting and the single crystal MgO disk (diameter of 2 inches) which carried out mirror polishing by the vacuum deposition, and it considered as

the substrate so that a <example 1> front face might turn into a field (100), and the ferroelectric thin film was formed in the following procedures on this substrate.
[0131] First, the above-mentioned substrate was fixed to the substrate electrode holder equipped with the rotation and the heating mechanism which were installed in the vacuum tub, and the vacuum tub was exhausted to 10-6Torr with the oil diffusion pump.
[0132] Subsequently, a substrate is heated at 600 degrees C and it is 20rpm. It was made to rotate. And the Pb-Gd-Ti multiple-oxide film (PGT thin film) of 300nm of thickness was formed by introducing radical oxygen gas at ten cc a rate for /from the source of efficient consumer response oxygen, and evaporating PbO, TiOx, and (x= 1.67) Gd from each evaporation source on a substrate. The supply from an evaporation source is PbO:Gd:TiOx. It carried out controlling so that a mole ratio is set to 2:0.1:1. That is, it was referred to as E (Pb/Ti) = 2.0.
[0133] When X-ray fluorescence investigated composition of the formed PGT thin film, it was (Pb+Gd)/Ti=1.02 and Pb/(Pb+Gd) =0.90. In this composition, since it is set to F (Pb/Ti) = 0.92, it is set to E (Pb/Ti) / F (Pb/Ti) = 2.2.
[0134] Evaluation by RHEED was performed about this PGT thin film. The RHEED pattern of this PGT thin film is shown in drawing 2 . The direction of incidence of the electron ray at this time was made into the [110] directions of a MgO substrate. As this result shows, the diffraction pattern of this PGT thin film front face is a pattern which is completely a streak. From this pattern and X diffraction evaluation, it has checked that the formed PGT thin film was a perovskite structure, and was an epitaxial film of c plane orientation. Moreover, it crosses throughout a surface simultaneously about this film, and they are ten places and JIS. When the ten-point average of roughness height Rz (a criteria length of L:500nm) by B0610 was measured, it was [on the average / in 6.3nm and the maximum] as flat as 1.3nm at 9.0nm and the minimum.
[0135] Cutting, and single crystal Si [p type 5ohm] disk of specific resistance (cm) (diameter of 2 inches) which carried out mirror polishing were used for the substrate so that a <example 2> front face might turn into a field (100). The front face which carried out mirror polishing performed etching washing by ammonium-fluoride solution 40%. It is ZrO2 by the procedure shown in the front face of this substrate below. A thin film (middle thin film) and BaTiO3 The thin film (insulating ground thin film) and the ferroelectric thin film were formed in this order. In addition, although an X diffraction and RHEED estimated each thin film, the sample with which evaluation was presented is taken out in the middle of a series of thin film formation processes in a vacuum tub, respectively. Also in the following examples, it is the same.
[0136] First, it is 20rpm about the substrate after fixing the above-mentioned substrate to the substrate electrode holder equipped with the rotation and the heating mechanism which were installed in the vacuum tub and exhausting a vacuum tub with an oil diffusion pump to 10-6Torr. It heated at 600 degrees C, having made it rotate and introducing oxygen near a substrate front face at 25 cc a rate for /from a nozzle. This formed Si oxide layer with a thickness of about 1nm.
[0137] Subsequently, 900 degrees C was made to heat and rotate a substrate. A rotational frequency is 20rpm. It carried out. Si surface treatment substrate equipped with the surface structure of 1x1 was obtained by supplying Zr from an evaporation source, introducing oxygen gas at 25 cc a rate for /from a nozzle at this time. The amount of supply of Zr was set to 5nm by thickness conversion of Zr oxide.
[0138] Next, it is ZrO2 of 10nm of thickness by supplying Zr from an evaporation source, where oxygen gas is introduced at 25 cc a rate for /from a nozzle, the substrate temperature of 900 degrees C, substrate rotational frequency 20rpm, and. The thin film was formed on the aforementioned processing substrate, and it considered as the middle thin film.
[0139] It is this ZrO2 as a result of an X diffraction. In a thin film, only a reflective (00L) peak is accepted, and the half-value width of a reflective (002) rocking curve is 0.7 degrees, and it turns out that it is the single orientation and the film of high crystallinity which are not in the former. In addition, although the peak (002) had lapped with Si (200) peak originating in a substrate, the above-mentioned half-value width is a value including Si (200) peak.
[0140] Furthermore, when RHEED measurement was performed about this thin film, the diffraction

pattern on the front face of a thin film is a pattern which is completely a streak, and has checked that this thin film was an epitaxial film from this pattern that is completely a streak. When Rz was measured like [thin film / this] the above, it is 0.08nm in 1.00nm and the minimum on an average at 0.80nm and the maximum, and it turns out on molecule level that it is flat.
[0141] In addition, ZrO2 It is ZrO2 when the stabilized-zirconia thin film was formed instead of the thin film. The same crystallinity as a thin film and front-face nature were obtained. Moreover, ZrO2 It is ZrO2 as a result of measuring the resistivity of the zirconium-oxide (YSZ) thin film stabilized by the thin film and Y. The thin film showed 5 times as much high resistance as a YSZ thin film, and excelling in insulation was checked.
[0142] Next, it is BaTiO3 of 50nm of thickness by supplying Ti from an evaporation source at a rate of Ba and1:1, where a nozzle to the substrate temperature of 900 degrees C, substrate rotational frequency 20rpm, and oxygen gas are introduced at 25 cc a rate for /. It is a thin film ZrO2 It formed on the thin film and considered as the insulating ground thin film.
[0143] This BaTiO3 When the X diffraction was performed about the thin film, only the peak (00L) was accepted and it has checked that the half-value width of a reflective (002) rocking curve was 1.4 degrees, and was the film of the high crystallinity in single (001) orientation.
[0144] When RHEED measurement of this thin film was carried out, a diffraction pattern is a pattern which is completely a streak, and it was checked that it is an epitaxial film.
[0145] Si substrate and ZrO2 A thin film and BaTiO3 The result of the X diffraction of each thin film which each orientation relationship of a thin film described above showed that they were BaTiO3/ (001)/ZrO2/(001) / Si (100). Moreover, as a result of performing RHEED measurement about each thin film as fixed in the direction of incidence of an electron ray, it is these RHEED measurement to BaTiO3. [100] //ZrO2 It has checked that they were [100]// Si [010].
[0146] Next, the PGT thin film of 300nm of thickness was formed like the example 1.
[0147] When X-ray fluorescence investigated composition of the formed PGT thin film, it was (Pb+Gd)/Ti=1.01 and Pb/(Pb+Gd) =0.89. In this composition, since it is set to F (Pb/Ti) = 0.90, it is set to E (Pb/Ti) / F (Pb/Ti) = 2.2.
[0148] Evaluation by RHEED was performed about this PGT thin film.
[0149] The RHEED pattern of this thin film is shown in drawing 3 . The direction of incidence of the electron ray at this time was made into the [110] directions of Si substrate. As this result shows, a RHEED pattern is a pattern which is completely a streak. From this pattern and X diffraction, it has checked that the formed PGT thin film was a perovskite structure, and was an epitaxial film of c plane orientation. Moreover, when Rz was measured like the above, it was [on the average] as flat as 0.9nm at 7.5nm and the minimum in 3.0nm and the maximum.
[0150] Pt electrode was formed in this PGT thin film front face, and it considered as MFIS structure. this -- the inside of the atmosphere -- setting -- 750 degrees C -- annealing during 10 minutes -- aluminum electrode of OMIKKU was formed in the substrate rear face the back the bottom, and the C-V property was evaluated A result is shown in drawing 4 . The hysteresis characteristic is obtained as shown in drawing 4 . a hysteresis band -- about 0.8 -- V it was . Next, this property was used and the element which used the ferroelectric thin film for the gate oxide film of FET was produced. It is 0.7V, when the gate voltage of FET was changed and the current between the source and a drain was measured. The memory window was obtained and non-volatile memory operation was checked. It was the the best for the gate type non-volatile memory which have MFIS structure to the dielectric constant of a PGT thin film being about 200, and ferroelectric thin films, such as the conventional PZT, being about 1000 since it is small.
[0151] On the same single crystal Si substrate as the <example 3> example 2, it is ZrO2. A thin film (middle thin film) and BaTiO3 The thin film (insulating ground thin film), Pt thin film (conductive ground thin film), and the ferroelectric thin film were formed in this order.
[0152] ZrO2 A thin film and BaTiO3 The thin film was formed like the example 2.
[0153] Subsequently, BaTiO3 The substrate which has a thin film on a front face was heated at 700 degrees C, and Pt thin film of 100nm of thickness was formed by the vacuum deposition method. It is

100W, introducing oxygen gas at three cc a rate for /, in order to prevent mixing of Pt (111) on the occasion of formation of Pt thin film. Rf plasma was introduced.

[0154] About this thin film, as a result of an X diffraction and RHEED estimating, it was checked that it is the epitaxial film of single (001) orientation.

[0155] Next, the PGT thin film with a thickness of 300nm was formed like the example 1.

[0156] When X-ray fluorescence investigated composition of the formed PGT thin film, it was (Pb+Gd)/Ti=1.07 and Pb/(Pb+Gd) =0.90. In this composition, since it is set to F (Pb/Ti) = 0.96, it is set to E (Pb/Ti) / F (Pb/Ti) = 2.1.

[0157] About this PGT thin film, RHEED evaluation was performed like the example 2. The obtained RHEED pattern is shown in drawing 5 . Moreover, the X diffraction view of this PGT thin film is shown in drawing 6 . In drawing 6 , since only the c-th page reflective peak of the perovskite structure of PGT was detected and the streak pattern was accepted in drawing 5 , it was checked that this thin film is an epitaxial film of single (001) orientation.

[0158] Next, it is ZrO2 on Si substrate like the above. A thin film and BaTiO3 After carrying out the laminating of a thin film and the Pt thin film, the ferroelectric thin film containing the rare earth elements shown in Table 1 was formed, and the membrane structure object sample was obtained. On the occasion of formation of these ferroelectric thin films, it was E (Pb/Ti)/F (Pb/Ti) =1.9-2.2. The abbreviated-name displays (PGT etc.) of the kind of ferroelectric thin film of each sample were shown in Table 1. In addition, in Table 1, the sample which has the above-mentioned PGT thin film is also indicated. Moreover, for comparison, it is the same structure and the sample which has a lead-titanate (PT) thin film as a ferroelectric thin film was also produced. Moreover, in order to perform comparison by the substrate, the sample which has PT thin film or a La addition PT (PLT) thin film on the substrate {the substrate which has Pt (001) orientation film on MgO} used in the example 1 was also produced. Composition of the ferroelectric thin film of each sample is shown in Table 1.

[0159] According to the X diffraction, the ferroelectric thin film of this invention sample is a perovskite crystal, orientation and orientation (100) were intermingled in sample No.14 (PPT thin film) (001), and it has checked that it was single orientation (001) with other this invention samples. Moreover, the RHEED pattern of the ferroelectric thin film of this invention sample was a streak-like. Therefore, it turns out that a crystallographic axis is very good and the ferroelectric thin film of sample No.14 has gathered within a film surface although orientation (001) and orientation (100) are intermingled, and it turns out that the ferroelectric thin film of other this invention samples is an epitaxial film.

[0160] The RHEED pattern and X diffraction view of a ferroelectric thin film of sample No.7 (PTT thin film) are shown in drawing 8 and drawing 11 , and the RHEED pattern and X diffraction view of a ferroelectric thin film of sample No.8 (PDT thin film) are shown for the RHEED pattern and X diffraction view of a ferroelectric thin film of sample No.2 (PPT thin film) in drawing 7 and drawing 10 at drawing 9 and drawing 12 , respectively.

[0161] sample No.2 [moreover,] (PPT thin film) -- the inside of the atmosphere -- setting -- 750 degrees C -- annealing during 10 minutes -- a next X diffraction view is shown in drawing 13 the bottom Comparison with drawing 10 and drawing 13 shows that the orientation (100) crystal appeared by annealing.

[0162] the ferroelectric thin film front face of each sample -- Pt electrode of 0.11mmphi -- forming -- the inside of the atmosphere -- setting -- 750 degrees C -- annealing during 10 minutes -- the bottom, the back, the lead was taken out from Pt thin film which is a conductive ground thin film, and the D-E hysteresis was measured by radiographic66A (radiant TEKINO logy company make) Consequently, the hysteresis was acquired with all this invention samples, and the ferroelectric polarization property was shown. It represents and the hysteresis curve of sample No.2 (PPT thin film), sample No.6 (PGT thin film), and sample No.7 (PTT thin film) is shown in drawing 14 , and 15 and 16, respectively. Moreover, the resistivity of the ferroelectric thin film which shows the remanence value Pr, the anti-electric field (polarization turn over voltage) Ec, and the leak property of each sample, and the polarization reversal defatigation property were measured. A result is shown in Table 1. In addition, a polarization reversal defatigation property is 106. Bias 0V after repeating batch pole reversal Polarization value Pr 1 Early

polarization value Pr 0 The ratio (Pr1 / Pr0) showed. The value of a defatigation property becomes small, so that degradation by polarization reversal is intense.
[0163]
[Table 1]

サンプル No.	種類	希土類元素Rn	(Pb+Rn)/Ti (モル比)	Pb/(Pb+Rn) (モル比)	抵抗率 (Ωcm)	2Ec (V)	2Pr (μC/cm²)	疲労特性 (%)
本発明例（Si基板）								
1	PLT	La	1.03	0.89	2.02×10^{11}	2.9	29	72
2	PPT	Pr	1.00	0.92	1.01×10^{11}	2.8	30	75
3	PNT	Nd	1.08	0.88	5.25×10^{10}	3.3	49	60
4	PST	Sm	1.06	0.91	1.43×10^{11}	4.1	48	63
5	PET	Eu	1.13	0.91	1.40×10^{11}	4.9	59	65
6	PGT	Gd	1.07	0.90	6.56×10^{10}	4.2	41	70
7	PTT	Tb	1.02	0.91	8.57×10^{10}	3.7	23	80
8	PDT	Dy	1.15	0.88	1.70×10^{11}	2.7	8.6	80
9	PHT	Ho	1.03	0.91	3.48×10^{10}	3.9	26	79
10	PErT	Er	1.15	0.87	8.50×10^{10}	2.7	6.8	90
11	PYbT	Yb	1.11	0.90	3.03×10^{10}	1.8	3.0	90
12	PYT	Y	1.11	0.86	9.32×10^{10}	2.5	8.5	90
13	PPGT	Pr, Gd	1.06	0.90	1.02×10^{11}	2.8	31	76
14	PPT	Pr	1.02	0.96	3.86×10^{10}	4.4	57.8	62
15	PPT	Pr	1.06	0.83	6.49×10^{11}	0.9	4.5	78
比較例（Si基板）								
16	PT	なし	1.06	1.0	1.99×10^{10}	6.2	60	45
比較例（MgO基板）								
17	PT	なし	1.01	1.0	リーク	測定不能	測定不能	測定不能
18	PLT	La	1.03	0.89	リーク	測定不能	測定不能	測定不能

[0164] this invention sample which has the ferroelectric thin film which added predetermined rare earth elements has succeeded in lowering Ec effectively compared with the comparison sample which has the lead-titanate thin film which has not added rare earth elements so that clearly from Table 1. Moreover, it turns out that this invention sample excels the comparison sample in the leak property and the defatigation property. Moreover, when the ferroelectric thin film which added La is formed on a MgO substrate, it turns out that leak is intense and a ferroelectric property is not acquired.
[0165] Although the dielectric constant of PT thin film (sample No.16) of the example of comparison shown in Table 1 was 510, the dielectric constants of the ferroelectric thin film of this invention sample shown in Table 1 were 196-626, and the low dielectric constant was fully obtained for the following [equivalent to PT thin film].
[0166] In addition, even when other metal thin films, such as Ir thin film, were used as an electric conduction ground thin film, the same result as the above was obtained.
[0167] Moreover, it is ZrO2 as a middle thin film. Even when what carried out the laminating of a thin film and the rare earth oxide thin film was used, the same result as the above was obtained.
[0168] Moreover, when applied to the record medium which mentioned above the membrane structure object produced in the above-mentioned example, the record reproduction by the AFM probe was possible.
[0169]

[Effect of the Invention] The ferroelectric thin film in this invention consists of lead system ferroelectric material which added predetermined rare earth elements, and can be applied to non-volatile memory, an infrared sensor, an optical modulator, optical-switch OEIC, a record medium, etc. by using the outstanding ferroelectric property. It is the the best for the record-medium use which records with the gate type non-volatile memory which has MFIS structure and MFMIS structure especially, and probes, such as AFM.

[0170] The manufacture method of this invention is the operating condition which enables realization of the thin film which has the outstanding ferroelectric property, and does not have the room of mediation of an impurity and which is easy to control, and can form a quality lead system ferroelectric thin film with sufficient repeatability over a large area with a diameter of 2 inches or more. And it is what enabled production of such a thin film on Si substrate which is a semiconductor application overlay important point, and utility value is industrially high.

[Translation done.]

PRIOR ART

[Description of the Prior Art] The electron device which formed the dielectric thin film on Si substrate which is a semiconducting-crystal substrate, and was integrated is devised. The dielectric separation LSI by still higher LSI of a degree of integration and SOI technology is considered by by combining a semiconductor and a dielectric. Moreover, the ferroelectric which is a kind of a dielectric is applicable to non-volatile memory by using polarization reversal, and since an infrared sensor, an optical modulator, optical-switch OEIC, etc. can be constituted, examination of a ferroelectric thin film material is advanced energetically. Moreover, application to the record medium with which a ferroelectric thin film records information using the polarization reversal by the AFM probe etc. is also considered. In the non-volatile memory and the record medium using polarization reversal of a ferroelectric, as a ferroelectric thin film material, a remanence value is large and what bears the repeat of record and read-out is needed.

[0003] Although the memory of the structure which used the ferroelectric for the gate of FET is devised as one sort of non-volatile memory, the memory which uses a ferroelectric for the gate has plentifully the point which should problem-etc.-solve the problem on production, and ferroelectric physical properties of thin film, and has not resulted in utilization as stated to electronic-intelligence communication society issue Shingaku Giho, SDM 93-136, ICD 93-130, (1993-11), and 53 pages. By this type of memory, although it is ideal to make a memory cell into metal-ferroelectric-semiconductor (MFS) structure, since realization is difficult, generally it considers as metal-ferroelectric-insulator-semiconductor (MFIS) structure or metal-ferroelectric-metal-insulator-semiconductor (MFMIS) structure. In such structures, in order to carry out polarization reversal of the ferroelectric and to carry out memory operation, you have to apply the electric field of sufficient intensity for a ferroelectric. With MFIS structure and MFMIS structure, since a ferroelectric and an insulator become equivalent to the series connection of a capacitor, in order to apply electric field to a ferroelectric enough, the device which lowers the dielectric constant of a ferroelectric and gathers the dielectric constant of an insulator is needed.
[0004] as the material of a present and ferroelectric thin film -- lead system oxides, such as $PbTiO3$, PZT ($PbZrO3$-$PbTiO3$ system), and PLZT ($PbZrO3$-$PbTiO3$ system by which La 2O3 was added), and Bi2 Ti2 NbO9 etc. -- it inquires by the polarization property excellent in Bi system oxide being shown
[0005] However, since a dielectric constant will become high about with 1000 if it thin-film-izes, when it uses as a ferroelectric thin film in the above-mentioned MFIS structure and above-mentioned MFMIS structure, it is difficult for PZT or PLZT to impress sufficient voltage.
[0006] On the other hand, it is PbTiO3. The dielectric constant in bulk is as small as about [100 or less] at a room temperature, and spontaneous polarization is 80microC/cm2 at the theoretical value of a bulk crystal. Compared with the material of other composition, a big value is shown wonderfully, and the Curie point is as high as 500 degrees C. That is, the most ideal value is indicated by the collection of data when thinking as a ferroelectric material of a memory use. Moreover, PbTiO3 Even when it thin-film-izes, a dielectric constant is as low as about 500. However, PbTiO3 Various troubles are becoming clear as a result of furthering the research and development which thin-film-ize and are made into an

electron device. the voltage Ec which carries out polarization reversal in the first place -- 85 kV/cm the fatigue property by polarization reversal, i.e., a repeat property, being bad to that leak arises in a thin film by being too high, the second crystal defect, semiconductor-ization, etc., and the third, and deteriorating in about 1000 times -- it comes out

[0007] In order to acquire a ferroelectric property, it is necessary to make it crystallize in the thin film material of the above-mentioned lead system oxide or Bi system oxide. the method of heating the temperature under thin film formation at 600 degrees C or more in order to make it crystallizing, and the method of annealing above 600 degrees C after membrane formation -- Jpn.J.Appl.Phys. -- 31, 3029 (1992), and Jpn.J.Appl.Phys. -- 33, 5244 (1994), and Mat.Res.Soc.Sympo.Proc. -- it is indicated by 243, 473 (1993), etc. However, Pb and Bi have high vapor pressure also in any of a metal and an oxide, and in order that they may evaporate in hot heat treatment and may cause a composition gap, a difficulty is in composition control.

[0008] Generally, in order to secure the device property optimal as a ferroelectric material, and its repeatability, it is desirable to use a single crystal. In the polycrystalline substance, it is difficult to obtain a good device property because of the disturbance of the physical quantity by the grain boundary. This is the same also about a thin film material, and a ferroelectric epitaxial film near the most perfect possible single crystal is desired. The same is said of the ferroelectric thin film in the non-volatile memory of the above-mentioned MFIS structure or MFMIS structure, and to be a dielectric epitaxial film near the most perfect possible single crystal is desired. Moreover, also in the medium (usually MFIS structure or MFMIS structure) which records using probes, such as AFM and STM, since the writing of a high-density bit will be attained if the ferroelectric epitaxial film near the most perfect possible single crystal is used, the realization is desired. Although it is necessary to grow epitaxially a metal thin film and a ferroelectric thin film on Si substrate which is a semiconductor substrate in order to realize a ferroelectric epitaxial film with MFIS structure or MFMIS structure, now, it does not realize yet.

[0009] With the ferroelectric material of a lead system, there is no composition gap and the thin film more near a single crystal is not obtained on the semiconductor substrate until now. Moreover, the ferroelectric material of a lead system of reactivity with Si used as a substrate will also be high, and it will have serious influence for the integrated-circuit property produced in Si substrate by diffusion of Pb to Si substrate.

[Translation done.]

DESCRIPTION OF DRAWINGS

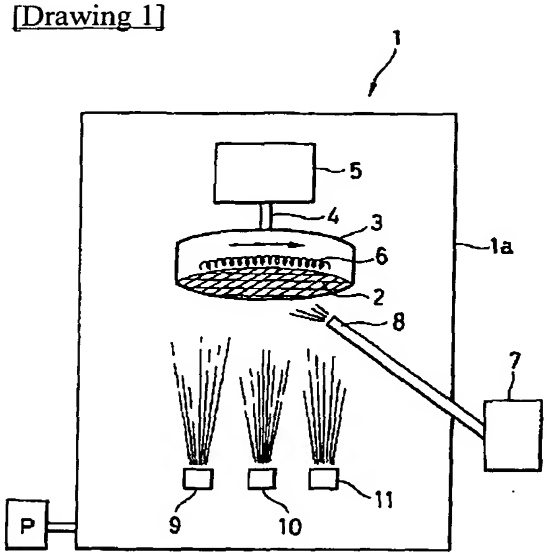
[Brief Description of the Drawings]
[Drawing 1] It is drawing showing an example of the vacuum evaporationo equipment used for the manufacture method of the ferroelectric thin film of this invention.
[Drawing 2] It is the drawing substitution photograph in which the crystal structure is shown, and is the RHEED pattern of the PGT thin film formed on Pt (001) thin film formed on the MgO (100) substrate. The direction of incidence of an electron ray is the MgO [100] direction.
[Drawing 3] It is the drawing substitution photograph in which the crystal structure is shown, and is the RHEED pattern of the PGT thin film formed on BaTiO3/(001)ZrO2 / (001) Si (100) structure. The direction of incidence of an electron ray is the direction of Si [110].
[Drawing 4] It is the C-V property of MFIS structure using the PGT ferroelectric thin film.
[Drawing 5] It is the drawing substitution photograph in which the crystal structure is shown, and is Pt (001)/. It is the RHEED pattern of the PGT thin film formed on BaTiO3/(001)ZrO2 / (001) Si (100) structure. The direction of incidence of an electron ray is the direction of Si [110].
[Drawing 6] Pt(001)/ It is the X diffraction view of the PGT thin film formed on BaTiO3/(001)ZrO2 / (001) Si (100) structure.
[Drawing 7] It is the drawing substitution photograph in which the crystal structure is shown, and is Pt (001)/. It is the RHEED pattern of the PPT thin film formed on BaTiO3/(001)ZrO2 / (001) Si (100) structure. The direction of incidence of an electron ray is the direction of Si [110].
[Drawing 8] It is the drawing substitution photograph in which the crystal structure is shown, and is Pt (001)/. It is the RHEED pattern of the PTT thin film formed on BaTiO3/(001)ZrO2 / (001) Si (100) structure. The direction of incidence of an electron ray is the direction of Si [110].
[Drawing 9] It is the drawing substitution photograph in which the crystal structure is shown, and is Pt (001)/. It is the RHEED pattern of the PDT thin film formed on BaTiO3/(001)ZrO2 / (001) Si (100) structure. The direction of incidence of an electron ray is the direction of Si [110].
[Drawing 10] Pt(001)/ It is the X diffraction view of the PPT thin film formed on BaTiO3/(001)ZrO2 / (001) Si (100) structure.
[Drawing 11] Pt(001)/ It is the X diffraction view of the PTT thin film formed on BaTiO3/(001)ZrO2 / (001) Si (100) structure.
[Drawing 12] Pt(001)/ It is the X diffraction view of the PDT thin film formed on BaTiO3/(001)ZrO2 / (001) Si (100) structure.
[Drawing 13] It is an X diffraction view after annealing of the PPT thin film of drawing 10 .
[Drawing 14] Pt(001)/ It is the D-E hysteresis characteristic of the PPT thin film formed on BaTiO3/ (001)ZrO2 / (001) Si (100) structure.
[Drawing 15] Pt(001)/ It is the D-E hysteresis characteristic of the PGT thin film formed on BaTiO3/ (001)ZrO2 / (001) Si (100) structure.
[Drawing 16] Pt(001)/ It is the D-E hysteresis characteristic of the PTT thin film formed on BaTiO3/ (001)ZrO2 / (001) Si (100) structure.
[Drawing 17] (a) is the ** type view showing the RHEED pattern of the surface structure of 1x1, and (b)

is the ** type view showing a RHEED pattern in case 2x1, 1x2, or these are intermingled.
[Description of Notations]
1 Vacuum Evaporationo Equipment
1a Vacuum tub
2 Substrate
3 Electrode Holder
4 Axis of Rotation
5 Motor
6 Heater
7 Oxidizing Gas Feeder
8 Oxidizing Gas Feed Hopper
9 PbO Evaporator
10 TiOx Evaporator
11 Rare-Earth-Elements Evaporator

[Translation done.]

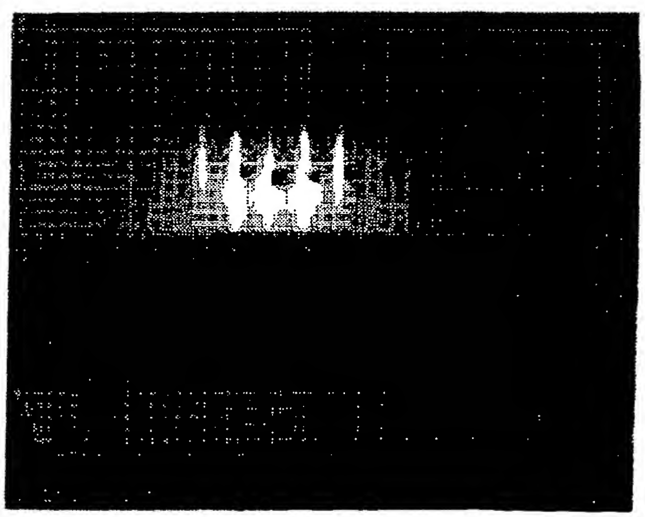
DRAWINGS

[Drawing 1]



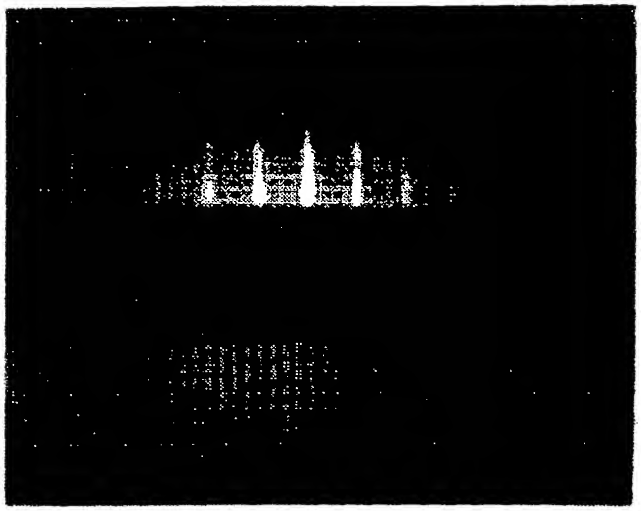
[Drawing 2]

図面代用写真



[Drawing 3]

図面代用写真



[Drawing 5]

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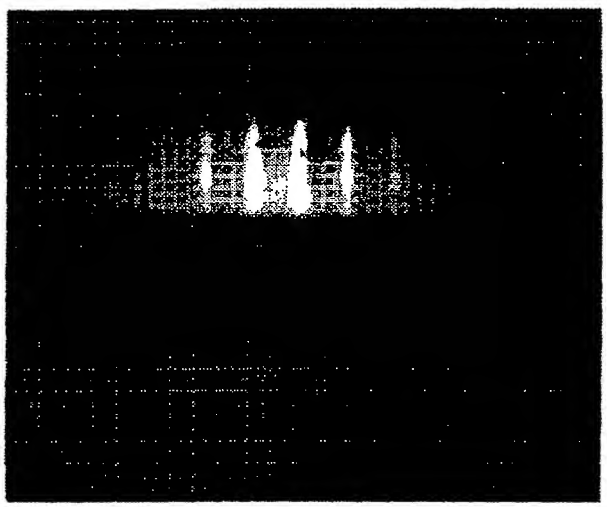
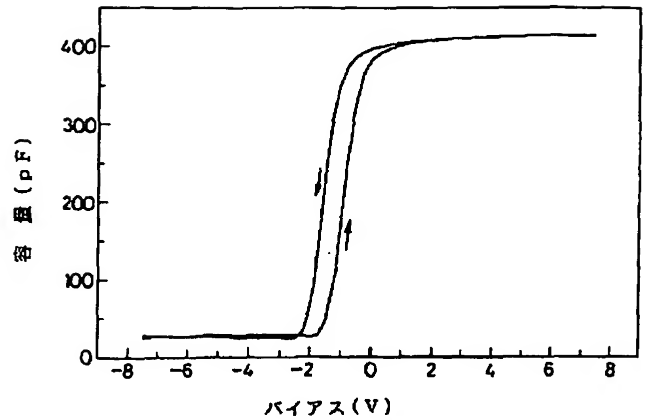
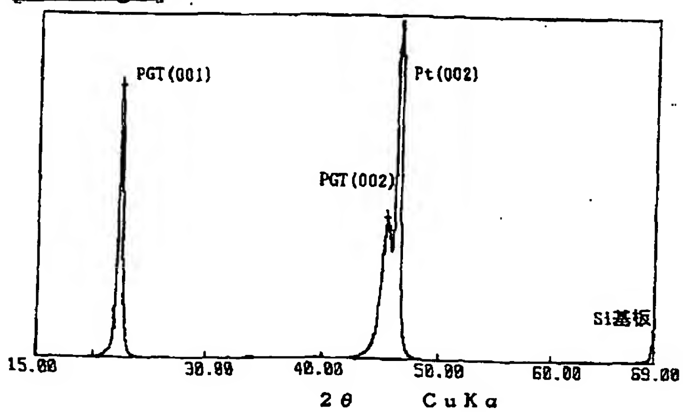


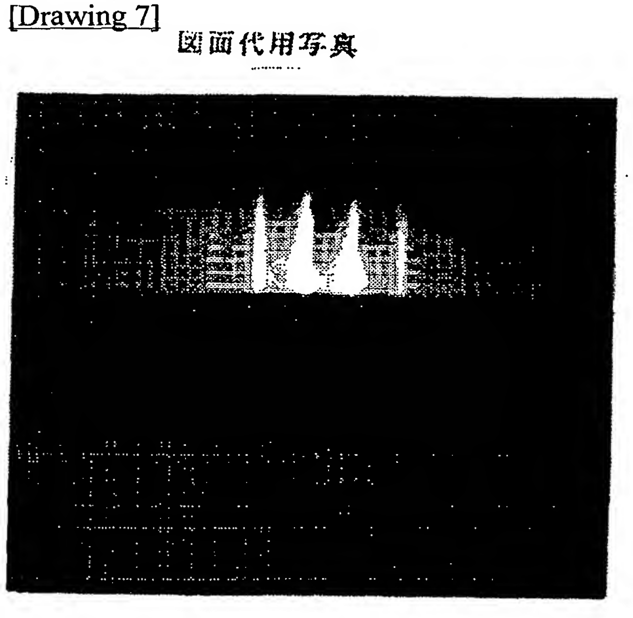
[Drawing 4]



[Drawing 6]

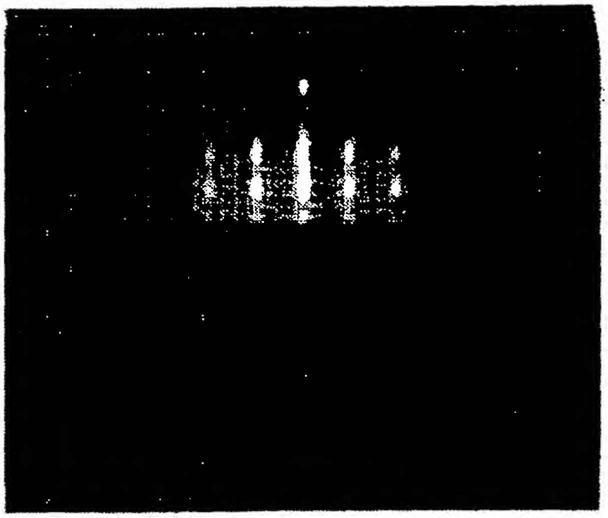


[Drawing 7]

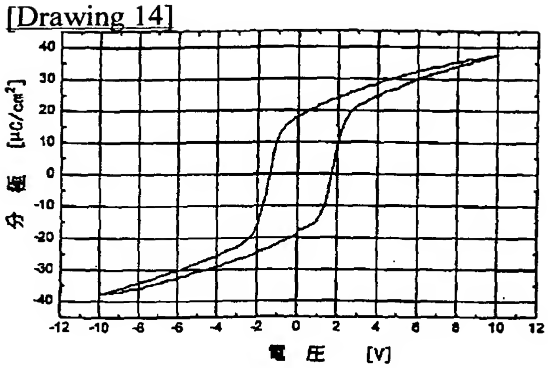


[Drawing 8]

図面代用写真



[Drawing 14]



[Drawing 9]

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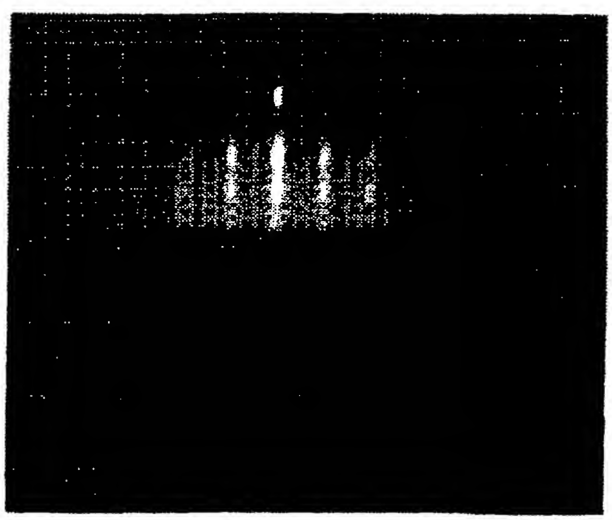
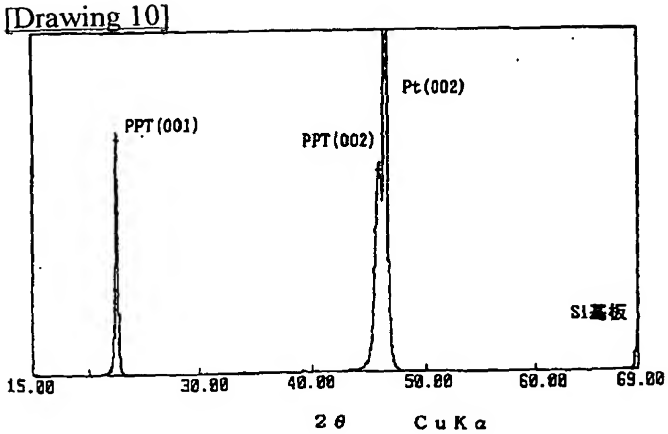
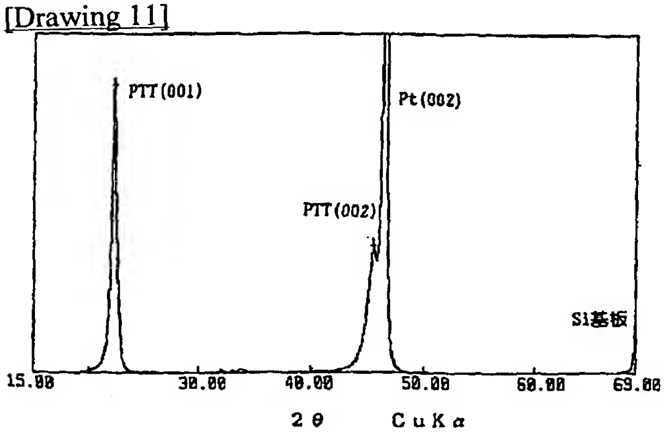


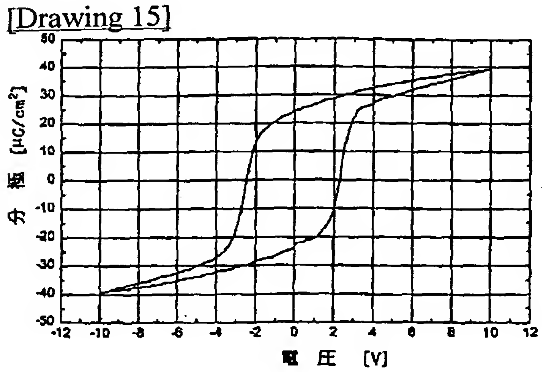
[Drawing 10]



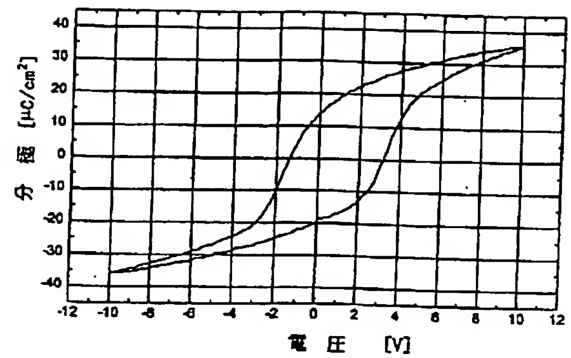
[Drawing 11]



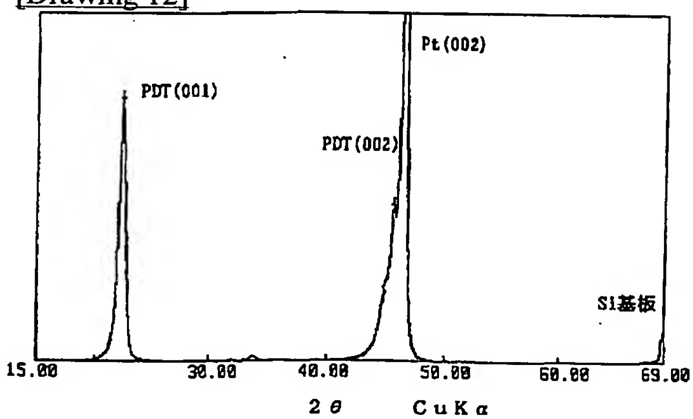
[Drawing 15]



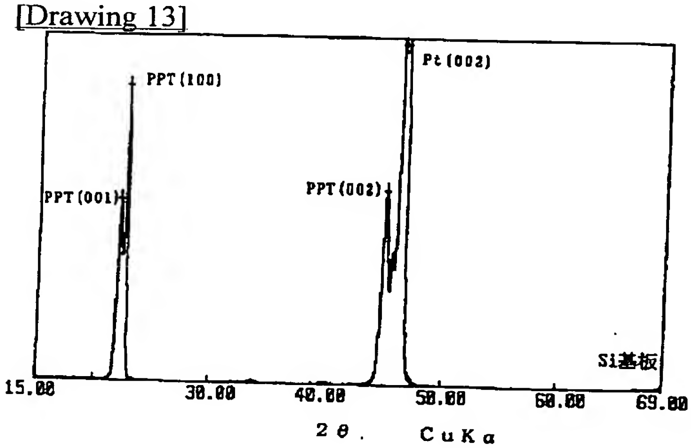
[Drawing 16]



[Drawing 12]

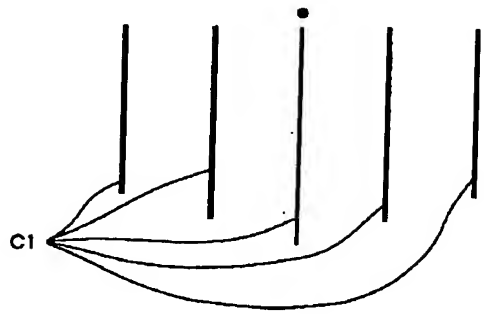


[Drawing 13]

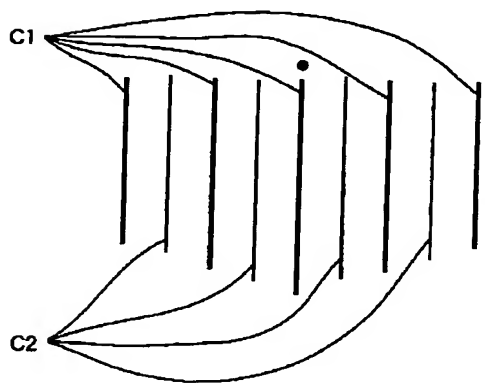


[Drawing 17]

(a)



(b)



[Translation done.]